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Potassium fixation in soils as affected by type of clay mineral, moisture conditions, and concentration of other ions

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NOTE TO USERS

POTASSIUM FIXATION IN SOILS AS AFFECTED BY TYPE OF CLAY MINERAL, MOISTURE CONDITIONS, AND CONCENTRATION OF OTHER IONS

by

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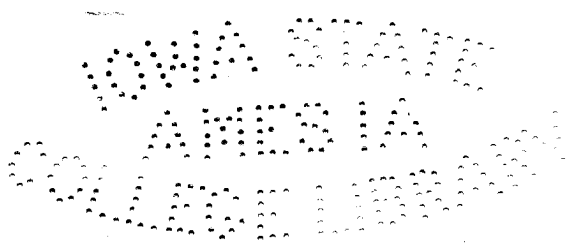

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INTRODUCTION

The term "fixation", as it is applied to potassium in soils, refers to the reversion of water-soluble potassium to difficultly soluble, nonreplaceable forms. It is generally considered that the water-soluble and replaceable soil potassium constitute the forms of this element that are most readily utilized by plants. The problem of potassium fixation, therefore, is of considerable practical importance in that it directly concerns the availability to plants of an essential nutrient often applied in fertilizers.

Numerous attempts have been made in the past fifteen years to explain the phenomenon of potassium fixation. Little progress was made, however, until it became known that the fixation occurred largely in the colloidal fraction of the soil and that this fraction consisted largely of certain definite clay mineral types which were distinctly concerned in the process. This discovery provided the impetus for several investigations aimed at disclosing the mechanisms involved in the fixation of potassium by certain of these clay minerals. The results thus far obtained have done much to create a better understanding of the processes which operate in the fixation of potassium. It is not possible, however, to distinguish, in every case, the various types of fixation which occur in soils. Moreover, there is a definite need for a better understanding

of the various factors which are concerned in potassium fixation. Much can be accomplished toward realizing these general objectives by further investigating the fundamental nature of potassium fixation in the clay minerals and in soils.

GENERAL SCOPE AND OBJECTIVES OF THE STUDY

In the present investigation, attention initially was centered around the so-called "high-lime" soils of Iowa due to certain peculiarities exhibited by these soils in fixing added potassium salts. Working with these soils, Allaway and Pierre (1) found that when potassium chloride was applied in amounts commonly employed in field practice, a high percentage of the potassium was converted to nonexchangeable form within a period of 24 hours under moist conditions. A considerable portion of the added potassium was fixed immediately upon contact with the soil.

The type of fixation which was found to occur in the calcareous soils of Iowa was particularly distinguished from the type which often had been reported for other soils in the United States, principally acid soils, in that no drying was required in order to bring about this rapid fixation. At the time this investigation was initiated, a large number of studies had been reported concerning the fixation which occurs in soils and minerals as a result of drying, and certain mechanisms had been proposed to account for this general type of fixation (45, 57). It had been reported that certain soils fixed potassium at a very slow rate when kept moist (63), but there had been no proposal advanced that this slow reversion of potassium to nonexchangeable form under moist conditions

was in any way related to the type which takes place very rapidly in moist soils. As a result of preliminary experiments with the high-lime Webster soils of Iowa, the possibility arose that the type of fixation which occurs rapidly in these soils and the relatively slow fixation of potassium in acid soils were concerned with the same type of mineral.

In one of the early experiments of the investigation, addition of ammonium salt was found to be a factor which greatly influenced the fixation of potassium by the calcareous Webster soils. The possible theoretical and practical importance of this finding in relation to the fixation of potassium in soils prompted further investigations designed to determine the underlying reason for the marked effect of ammonium on potassium fixation.

The investigations reported herein were carried out with the general objective of characterizing the processes responsible for the fixation of potassium which occurs under moist conditions and on drying in soils. The specific objective of chief importance, however, was to determine the mechanism which operates in causing potassium to become nonexchangeable under moist conditions. In attempting to achieve these goals, a number of studies were conducted with the soils concerned and with the types of clay minerals known to occur in these soils.

HISTORICAL

Early Investigations on Potassium Fixation in Soils

Some of the early attempts to account for the disappearance of soluble potassium applied to soils over a period of years revealed that leaching and removal by crops accounted for only a part of the loss in so-called "available" potassium. As early as 1894, Dyer (14) at Rothamsted concluded that the potassium soluble in one percent acetic acid together with that removed by crops accounted for only about half of the 4,084 pounds of potash per acre which had been applied over a period of 38 years.

Frear and Erb (16) also determined the amounts of potassium recovered from fertilizer applications in a study of the potassium economy in soils. During a 36-year period in which 1800 pounds of potash per acre had been applied, they found that about one-fourth of the potassium had been removed by crops. At the end of the period, only about one-sixth of the total application was soluble in fifth normal HCl. It was concluded that the remainder had become fixed in relatively insoluble forms. A study later reported by Page and Williams (46) in 1925 left little doubt that fixation of potassium in nonexchangeable form is a factor to be reckoned with in potash fertilizer practices.

Development of Concepts Regarding the Nature of Potassium Fixation

Before much was known about the manner in which potassium becomes fixed in soils, it was recognized that there was a tendency for equilibrium to be established between the various forms of soil potassium. Bartholomew and Janssen (4) and Hoagland and Martin (22) were among the first to suggest this possibility. Later studies by Wood and DeTurk (63), dealing with the length of time required for fixation of added potassium to reach a constant value in soils demonstrated the complexity of the equilibrium between the different forms of soil potassium.

Volk's (59) classic attempt to reveal the nature of potassium fixation in soils provided the impetus for a large number of studies which followed during the succeeding 10-year period. His work confirmed the conclusion reached by Frear and Erb (16) in 1918 that the fixation of potassium largely occurs in the colloidal fraction of soils. Moreover, Volk was the first to investigate the importance of drying in bringing about potassium fixation. Thus, he found that when soils were kept moist continuously, little or no fixation occurred; but when the soils were alternately wetted and dried, there usually was a rapid and pronounced fixation of potassium in a non-replaceable form. On drying, 100 soils, each receiving 1000 pounds of potash per acre, showed a capacity to fix potassium

varying from zero to all that was added. Considerable controversy has existed concerning Volk's (59) final conclusion that "a portion of the added potassium reacted with colloidal silicates and became fixed in the form of muscovite, thus converting added available potassium into difficultly available form". The formation of muscovite was pictured as involving the formation of the new mineral by reaction between various soil constituents, rather than the reformation of a mineral already existing in the soil. Joffe, et al. (27) believed that it was unlikely that muscovite would be formed upon the addition of potassium under the conditions of temperature and pressure which prevail in the soil as it exists in the field.

Joffe and Kolodny (27) were able to synthesize some rather ill-defined, insoluble potassium complexes by adding a potassium chloride solution to various phosphates of iron, aluminum, calcium and magnesium, followed by drying. They concluded that this was one of the principle mechanisms accounting for fixation of potassium in soils. In a later study, (26) they modified their viewpoint concerning the importance of phosphates, stating that other soil constituents might also be responsible in part for the conversion of potassium to difficultly soluble forms. Apparently, Joffe no longer believes that phosphate compounds in the soil are of importance in potassium fixation, since in a recent series of papers (28, 29, 30, 36, 37) no mention is made of the phosphate-potassium relationship.

G. W. Volk (58) reinvestigated some of the earlier findings of N. J. Volk (59). Besides reaffirming the earlier conclusions, this worker concluded that alumina and, in some instances, silica were involved in the fixation of potassium which occurs on drying. The view that muscovite was formed in some obscure manner by reaction between aluminates, silicates, and potassium received further emphasis. He found, however, that certain minerals, e.g., muscovite, bentonite, and sericite, fixed varying amounts of added potassium when subjected to wetting and drying. Volk's (58) view may be expressed by referring to one of his conclusions drawn from an experiment in which it was shown that extraction of a soil with Na_2CO_3 caused a marked increase in its capacity to fix potassium. From this study, he concluded that extraction with the alkaline solution caused formation of sodium aluminate and/or sodium silicate which then reacted with the soil to form difficultly soluble compounds.

In 1936, Chaminade and Drouineau (11) and Chaminade (10) reported a number of significant experiments which seem to have received scant attention from American workers. The views which the latter worker presented mark the beginning of a new concept regarding the nature of potassium fixation which was quite unlike the viewpoints cited above. Chaminade and Drouineau (11) drew the conclusion, based on evidence obtained from grinding various soils and minerals, that "fixation is the penetration of cations into the interior of the

crystal lattice". It was not until several years later that this concept was expressed by other workers (63). Thus, the idea that certain specific minerals were responsible for fixation of potassium in soils was developing.

From 1937 to the present time, much emphasis has been placed on the importance to potassium fixation of the clay minerals existing in the soil colloidal fraction. A number of investigations have been carried out using bentonite clay, consisting predominantly of montmorillonite, a clay mineral known to occur in soils. Grim (19) has compiled an extensive review of the literature dealing with this important clay mineral. Volk (58) showed that "white bentonite" was capable of fixing far more potassium than any of the other minerals tested. Shortly thereafter, Truog and Jones (57) confirmed the fact that bentonite was high in its fixing capacity. They found upon drying bentonite clays which were previously saturated with potassium, that from 15 to 50 milliequivalents of potassium per 100 grams of clay became fixed in difficultly soluble form. On the other hand, kaolinite and halloysite which are members of another group of clay minerals (19) fixed no potassium. It was found that the exchange capacity of various bentonites was reduced due to potassium fixation by an amount equivalent to the potassium fixed. This significant finding laid the ground-work for a better understanding of the manner in which potassium becomes fixed by minerals of the

montmorillonite group. Other workers (31, 33, 40) have confirmed these results. The view expressed by Truog and Jones (57) that potassium becomes "trapped" between the expanding layers of montmorillonite when drying occurs is essentially the same as the view held today by many workers. However, further advancement has been made in clarifying the mechanism involved.

Joffe and Kolodny (26) preheated a series of samples of a montmorillonite clay to temperatures ranging up to 600 degrees C. and found that at temperatures above 500 degrees, no fixation of potassium took place. Since the property of lattice expansion disappears simultaneously with the loss in fixing capacity due to heating, it was further indicated that the existence of the flexible lattice structure in minerals of this group was in some manner concerned with their ability to fix potassium.

Further light was thrown on the mechanism of potassium fixation in minerals of the expanding lattice type by the work of Page and Baver (45). Their studies brought out the importance of considering ionic size in relation to fixation of potassium and other cations. They postulated that the empty spaces existing between the expanding layers of montmorillonite might, by virtue of their size, be considered as the loci of potassium fixation. These empty spaces are the center of hexagonal oxygen rings which are part of a continuous network. The effective diameter of each space is 2.8 Angstrom

units. They demonstrated in an indirect manner that this mineral was capable of fixing cations which possess ionic diameters close to the size of these spaces. Thus, K^+, Rb^+, NH_4^+, and Cs^+ with ionic radii of 1.33, 1.48, 1.21, and 1.67 respectively, are fixed in relatively larger quantities than are such ions as Ca^{+2}, Mg^{+2}, and Na^{+1} having much smaller radii. Fixation did not occur, however, except on drying which shows that the closing of the sheets upon dehydration is an essential part of the mechanism.

The fixation of potassium by secondary micaceous minerals has not been studied extensively, although it is generally believed that these minerals play a part in the conversion of potassium to nonreplaceable forms. Muscovite, a primary mica, was considered by Volk (59) to be the end-product of potassium fixation in soils. Later, G. W. Volk (58) determined the amounts of potassium fixed by several muscovites which varied in their original contents of potassium and found that generally very small amounts became nonexchangeable upon drying the ground minerals after adding potassium. Certain of these muscovites fixed appreciable quantities of potassium after being treated with carbonated water or Na_2CO_3 solution. A sericite, now termed illite (19), likewise fixed potassium after being treated with Na_2CO_3, but fixed none prior to this treatment. The significance of the increases noted after extraction with this alkaline solution or with carbonic acid was not evident, although it was believed to be related to the formation of

sodium aluminate. Joffe and Levine (28) found that a sericite fixed potassium after being electrodialyzed but not prior to this artificial "weathering".

Chaminade and Drouineau (11) showed that glauconite, a secondary mica, had fixed appreciable quantities of potassium one month after the potassium salt was added to a suspension of the mineral. This finding, however, has gone largely unnoticed.

Schachtschabel (52) for several years has placed great emphasis on the importance of the micaceous minerals as the "storehouse" of potassium potentially available to plants. He considers this form to be much more important in this respect than any other of the difficultly soluble forms found in the soil. In 1937 (52), he found that a soil which before cropping did not fix added potassium either when moist or dried, absorbed large quantities in the nonexchangeable form after being heavily cropped (5 Neubauer plantings). He attributed this change in the capacity to fix potassium solely to the presence of micas in the soil. Thus, he presents the view that the intensive cropping caused large amounts of potassium to be released from the micas, and that the potassium lost in this manner was replenished upon adding more potassium. It is of particular interest as will become more evident later that the "refixation" of potassium occurred in moist soil. The conclusion of Schactschabel is much the same as was expressed by Wood and DeTurk three years later (63).

The latter workers concluded from their studies that fixation in soils containing the illite type of clay mineral is a process of "reforming an old mineral rather than creating a new one". Later work by Schachtschabel (53) has added emphasis to his former viewpoint that potassium lost from the "intramicellar" positions of micas may be replenished by "intramicellar exchange" as he refers to the process. The reports by Denison, et al. (12), Joffe and Levine (28), Gruner (20, and Bray and DeTurk (8) contain evidence that fixation of potassium by micaceous minerals takes place after loss of part of the potassium through weathering.

Biological fixation of potassium has been considered in a few instances to be of importance in soils. Jenny and Shade (25) concluded that increased fixation of potassium due to liming might result from stimulated biological activity. Blume and Purvis (6) believed that biological activity accounted for a part of the fixation of potassium noted in their experiments. More recently, Hurwitz (24) presented some rather conclusive evidence that fixation of potassium occurs in living microbial tissue under certain conditions. It seems quite clear from his studies, however, that such fixation requires the presence of large amounts of energy material to provide food for a vigorous microbial population. Moreover, there is a marked fluctuation in the amounts of potassium immobilized in this manner as evidenced by measurements made over a considerable period of time. Microbiological activity as a factor

causing immobilization of potassium appears to have been a very minor factor in most studies on potassium fixation, since in only a few instances has energy material been supplied. Furthermore, in the studies where drying at elevated temperatures occurred, it can be assumed that microbial activity was very low.

Factors Which Influence the Amounts of Potassium Fixed by Soils

The principle types of clay minerals which are known to be capable of fixing potassium have already been indicated. These appear to be minerals of the montmorillonite and illite groups. It is evident that the amounts of these clay minerals present has much to do with the capacity of soils for fixing potassium. The work of Page and Baver (45) emphasized the importance of drying in the fixation by minerals possessing the expanding type of lattice. Some instances have been cited which indicated that fixation under moist conditions might be attributed to micaceous minerals. The importance of defining the moisture conditions under which studies dealing with potassium fixation are carried out becomes quite clear.

A number of different procedures involving various moisture conditions have been followed in studying potassium fixation. The practice of alternately wetting and drying the soil or mineral at elevated temperatures originated with Volk's

work (59), and has been followed by a number of workers (15,18,21,26,27,28,29,30,31,33,36,37,43,45,57,58,59). In certain instances, the capacity to fix potassium was determined on soils which had been stored moist and were air-dried before analysis (23,63,64). It was considered that air-drying had no effect on the amount of K fixed. However, the effect of air-drying on fixation of potassium cannot be disregarded, as shown by Volk (59), Attoe and Truog (3), Attoe (2) and Martin et al. (40). These workers have shown that while no fixation may occur during moist storage of soils with added potassium, appreciable amounts may become nonexchangeable when the soils are allowed to dry at room temperature. Attoe's (2) study is very specific in showing that as the relative humidity of the atmosphere in which samples receiving potassium are stored decreases from 100 per cent to rather low values, fixation increases markedly after long periods of contact. Chaminade (10) also has shown that fixation is greater when the relative humidity of the surrounding atmosphere is lowered.

Several workers have studied fixation of potassium when samples unquestionably were maintained moist throughout the period of contact between added potassium salt and soil or mineral. In certain instances (1,2,11,22) marked fixation occurred, while in others (2,3,10,11,52) no fixation occurred under moist conditions. As shown by Allaway and Pierre (1), certain calcareous soils fix a large proportion of added potassium under these conditions.

On reviewing the literature concerned with potassium fixation, it becomes immediately apparent that several outstanding results have been obtained which have gone without explanation. Some of these findings which bear an important relation to the present investigation will be discussed briefly.

In certain instances, cations other than potassium may become fixed in nonexchangeable form. Page and Baver (45), Chaminade (9), Chaminade and Drouineau (11), Martin, et al. (40), Truog and Jones (57), Gruner (20), and Joffe and Levine (29) are the principal workers who have demonstrated this. As has been mentioned previously, the ions which have ionic radii somewhat similar to that of potassium are particularly susceptible to being fixed. That ions which have radii much smaller than that of potassium are fixed at all has been questioned (29), although Prince, et al. (50) found evidence that magnesium was fixed to some extent in New Jersey soils. The importance in the present study of considering other ions which are susceptible to being fixed is readily seen, if it is true, as has been suggested (29,45) that the same positions are involved for all of the ions concerned.

Large organic cations with radii much greater than that of potassium are not "fixed" in the sense that they become nonexchangeable. Yet, as shown by Page and Baver (45), the presence of these organic cations markedly reduces fixation on drying by the montmorillonite type of mineral, presumably because these ions prevent the flexible layers from closing and

"entrapping" potassium ions. It is logical to assume that such large ions would have little effect on fixation by micaceous minerals possessing fixed lattices, since they would be unable to enter between the sheets due to steric limitations. Whether there are present in the soil any organic compounds which influence potassium fixation in the manner indicated for montmorillonite is not known, although such a suggestion would not seem to be unreasonable (55).

Another problem which has not been solved deals with the effect of liming on fixation of potassium. In general, the early work done on this subject indicates that liming may increase the capacity of the soil to fix potassium (38,39). The literature on the subject has been reviewed quite thoroughly in recent publications (49,66). Gilligan (18) has presented striking evidence that liming greatly increased fixation of potassium in certain soils. However, lime had no effect on the amount of potassium fixed by a Portsmouth loam. York and Rogers (66) have presented recent evidence that liming tends to release potassium from certain potassium-bearing minerals present in soil, while, at the same time, tending to increase fixation of the potassium added. They concluded from certain studies where there was no apparent effect of liming on fixation of added potassium that actually liming had increased fixation, since these soils showed release of this element when limed without addition of potassium. Whether the influence of lime on potassium fixation is direct or is concerned with the increase in pH which follows liming

is not clear, as has been discussed by Joffe and Levine (30).

It was first noted by N. J. Volk (59) and later confirmed by G. W. Volk (58) and others (40) that extraction of certain soils and minerals with Na_2CO_3 solution often markedly increased the capacity of these materials to fix potassium on drying. No explanation has yet been offered which adequately accounts for the increases noted.

The relation of exchange capacity of the fixing material, whether soil or mineral, to the amount of potassium fixed has received considerable emphasis in recent papers by Joffe and Levine (28,29,30) and Levine and Joffe (36,37). Included are reports of various experiments in which an attempt has been made to show that the exchange capacity is the chief factor which determines the amount of potassium fixed by soils and different types of clay minerals. The general conclusion reached by these workers was that "the phenomenon of fixation is essentially the same for different fixing materials." It seems, however, from a consideration of the large amount of published information dealing with potassium fixation, that such oversimplification of the problem is not justified.

A few workers have shown that addition of phosphate along with the potassium may increase fixation of potassium (27, 63, 64, 65). Tressler (56) noted that soil potassium was much less soluble in a saturated solution of monocalcium phosphate than in other salt solutions, which suggests that fixation of potassium was induced by the addition of phosphate. It has also

been noted (27,65) that field plots which had received acid phosphate fixed more potassium than those which had not been fertilized with phosphate. The practical or theoretical significance of these findings dealing with phosphate-potassium relations has not yet been established.

FIXATION OF POTASSIUM IN SOILS UNDER MOIST CONDITIONS AND ITS RELATION TO AMMONIUM FIXATION

The first phase of the problem consisted of a series of experiments designed to differentiate the process by which potassium is rapidly fixed under moist conditions from that responsible for the fixation which occurs on drying. The amounts of potassium fixed by each of the two processes under various conditions was determined, and the effect of certain treatments upon each type of fixation was investigated. During the course of these experiments, it appeared that ammonium fixation might be taking place through mechanisms similar to those responsible for potassium fixation. For this reason a series of experiments comparing ammonium and potassium fixation and a study of the interaction of these two ions in fixation processes were included in the investigation.

In every case, the fixed potassium is defined as that which was retained by the soil against leaching with large quantities of normal ammonium acetate. Fixed ammonium was defined as that which could not be removed by leaching the soil with normal potassium chloride.

Materials and Methods

Soils used in studying fixation of potassium and ammonium

Certain information concerning the soils used in this study is given in Table 1. All samples were obtained from plots of outlying field experiments during the period 1939 to 1943. In every case, the samples represent the plow layer, 0 to 6 inches in depth. The parent material of the Clarion-Webster soil area is the Mankato substage of the Wisconsin glacial till. Carrington soils were derived from Iowan substage till. The remainder of the soils included were developed from loess of varying depth.

Certain soils which are intermingled with the Webster series contain considerable amounts of free carbonates. Since these soils comprise relatively small areas, they have not been distinguished in soil survey maps from the associated normal Webster soils because of the intricate pattern involved. These so-called "high-lime" soils have been studied more extensively than other soils in the present investigation. The Webster soil, BL1, has received particular attention, since this soil is unusually deficient in "available" potassium as determined from field response to potash fertilization. Other Webster soils which were found to be quite deficient in available potassium as shown by field studies with corn are 25A, 32AH, 29A, and 38A. Corn growing on the remaining Webster soils

Table 1

Soils used in studies on K and NH_4 fixation.

File No.	Soil	Great Soil Group	pH or CCE*	Year Sampled	Location	
					County and/or	Farm
25A	Webster silty clay loam	Wiesenboden***	18%	1939	Humboldt	Warland
26A	Webster silty clay loam	Wiesenboden	11%	1939	Humboldt	Warland
37A	Webster silty clay loam	Wiesenboden	2%	1939		Holdgrafer
32AH	Webster silty clay loam	Wiesenboden	22%	1939		Holdgrafer
28A	Webster silty clay loam	Wiesenboden	pH 7	1939	Humboldt	Johnson
29A	Webster silty clay loam	Wiesenboden	pH 7.2	1939	Humboldt	Johnson
34A	Webster silty clay loam	Wiesenboden	14.7%	1939	Wright	Benson
BL6	Webster silty clay loam	Wiesenboden	pH 7.2	1939	Hancock	
24A	Webster silty clay loam	Wiesenboden	C**	1939	Polk	Moeckley
38A	Webster silty clay loam	Wiesenboden	20%	1939	Wright	Benson
BL1	Webster silty clay loam	Wiesenboden	pH 7.5	1942	Hamilton	Goring
BL2	Clarion loam	Prairie	pH 5.2	1942	Agronomy Farm, Iowa Agr. Experiment Sta.	
619	Marshall silt loam	Prairie	pH 5.3	1942	Sioux	
BL4	Carrington loam	Prairie	pH 4.8	1942	Linn	
100	Clinton silt loam	Gray-brown (podzolic)	pH 6	1942	Louisa	Sands
626	Clinton silt loam	Gray-brown (podzolic)	pH 5.3	1942	Louisa	
603	Fayette silt loam	Gray-brown (podzolic)	pH 5.9	1940	Fayette	

*CCE = % carbonates equivalent to $CaCO_3$ (approximate).
**C = calcareous (CCE not determined).
*** - Tentative

appeared to be normal in that little or no marginal "firing" of the leaves was evident during the year in which the soil samples were taken. The available potassium status of the other soils in Table 1 ranges from "border-line" to plentiful as indicated by field studies

Methods of studying fixation of potassium and ammonium

Potassium fixation. The choice of a procedure to be used in determining the capacity of soils to fix potassium is somewhat arbitrary and depends upon the objectives sought, as evidenced by the numerous procedures which have been followed by various workers.

In the present study, fixation under moist conditions took place in stoppered flasks using water suspensions or pastes. Usually 10-gram samples of soil were weighed and placed in Erlenmeyer flasks, after which the desired quantity of standard KCl solution was added. In certain instances, a particular soil:liquid ratio was secured by adding a definite quantity of distilled water. The amount of potassium fixed was determined after a definite period of contact between the soil and potassium solution. The majority of experiments involving fixation under moist conditions were carried out using 30-minute or 48-hour periods of contact. The time of standing after addition of the potassium salt and any variations in the general procedure outlined above will be indicated in presenting the results of the experiments concerned. No control over tem-

perature during incubation was maintained; however, various results obtained over an extended period indicate that temperature changes encountered in the laboratory (approximate range, 24 to 30 degrees C.) do not significantly influence the amounts of potassium becoming nonexchangeable.

In determining the fixation of potassium which occurs on drying, the oven temperature at which samples were dried was 95 degrees C. The samples were alternately wetted and dried six times.

Ammonium fixation. Fixation of ammonium was determined after adding standard NH_4Cl solution to the soil samples and allowing the suspension or paste to stand for a definite period of time. The soil:liquid ratio was controlled in all experiments, and it usually ranged from 1:1.5 to 1:2.5.

The possibility that ammonia might be lost by volatilization upon addition of NH_4Cl to calcareous soils was investigated. A simple experiment was conducted in which the air above the soil-water-NH_4Cl system was withdrawn periodically into HCl during a 24-hour incubation period, and the HCl was tested for ammonium with Nessler's reagent. It was found that no ammonia volatilized at room temperature with the concentration of NH_4Cl added (2.5 m.e. per 100 grams).

The possibility that microbiological activity might influence the results obtained in studying fixation of ammonium ions led to another preliminary experiment, the results of

which are shown in Table 2. These data show that during an incubation period of 120 hours, fixation was approximately the same whether the soil was partially sterilized or untreated. On the basis of the evidence obtained, it was concluded that no pretreatment of soil was necessary in studying fixation of added ammonium under moist conditions. However, in order to minimize the likelihood of error due to microbial action, 3 to 4 drops of toluene were added to samples in subsequent studies. Moreover, the longest period of incubation employed in later experiments was 48 hours; in most cases, fixation was measured after 30 minutes of contact with the added NH_4Cl.

Chemical methods

Determination of potassium fixation. The extractant used to recover exchangeable and water-soluble potassium was normal ammonium acetate (pH 6.8). It was found that extraction of a 10-gram sample of soil with 250 ml. of this reagent ensured removal of all except traces of these forms of potassium. Samples were first shaken for one hour with 100 ml. of the extracting reagent. Then they were filtered through Buchner funnels, followed by leaching with successive 25-ml. portions of the extractant applying slight suction. In one experiment, extraction was accomplished using centrifuge tubes and centrifuging to clarify the extracts. The procedure devised by Lawton (35) for determining potassium was used in the 1946-1947

Table 2. The fixation of NH_4 under moist conditions by a calcareous Webster soil (38A) as affected by refrigeration, addition of toluene, and autoclaving.

Prior treatment or conditions during incubation	Time of incubation (hours)	NH_4 Added as NH_4Cl (m.e./100g.)	NH_4 Fixed (m.e./100g.)
Untreated, incubated in laboratory, 25°C	120	12.24	1.07
Autoclaved before NH_4 added; incubated in laboratory, 25°C	120	12.24	0.93
Untreated, incubated in refrigerator, 0-5°C	120	12.24	1.14
Toluene added; incubated in laboratory, 25°C	120	12.24	0.94

*Exchangeable NH_4 = 0.36 m.e. per 100g; extractant, N KCl; recovery of NH_4 determined by distillation of the KCl extract and titration; sample weight = 20g.

studies and was adhered to without modification. In a few earlier experiments done in 1941, the method of Brown, Robinson, and Browning as modified by Allaway and Pierre (1) was used. It was found that the two methods gave similar results on soil extracts, which is in agreement with Lawton's (35) conclusion. Results of potassium analyses are expressed as milliequivalents per 100 grams of oven-dry soil.

Determination of ammonium fixation. Since only a few studies have been reported in the literature relating to ammonium fixation in soils, a somewhat detailed account of the methods which were used will be presented.

The kind of extractant to employ in recovering water-soluble and exchangeable ammonium was investigated before undertaking detailed studies on fixation of ammonium. Various extractants commonly used in studies on base exchange were compared. Olsen's (44) method for extracting exchangeable ammonium was discounted, since it involves extracting the soil with a strongly acidic reagent (KCl-HCl) which undoubtedly attacks nonexchangeable as well as exchangeable ammonium. The results in Table 3 show that the amounts of ammonium fixed were nearly the same, as measured by recovery with the different solutions of neutral salts. It is quite possible that the somewhat greater recovery using barium acetate is significant, since in all cases duplicates agreed very closely. Normal KCl was adopted as the extractant in subsequent studies. This choice

Table 3 Recovery and fixation of NH_4 added to a Webster soil (24A) using different extracting reagents.*

Extractant	NH_4 added as NH_4Cl (m.e./100g)	Replaceable NH_4 (m.e./100g)	NH_4 Extracted (m.e./100g)	NH_4 Fixed (m.e./100g)
N KCl	12.18	0.26	11.69	0.75
N Ca-Acetate	12.18	0.26	11.63	0.81
N Ba-Acetate	12.18	0.26	11.80	0.64
N Na-Acetate	12.18	0.26	11.71	0.73

* 20g. samples used. Leached with 500 ml. of extracting solution after moist incubation for 42 hours following addition of NH_4Cl.

was based partly on the fact that potassium and ammonium ions possess nearly the same ionic radii (45). The method of extraction was essentially the same as has been described in a previous section for potassium studies on fixation. Leaching on the Buchner funnels was continued until the leachate no longer gave a test for ammonium ion with Nessler's reagent. In most cases, 250 ml. of the normal KCl were sufficient.

In early experiments to determine ammonium fixation, 20-gram samples were used. The ammonium recovered by KCl extraction was distilled into standard HCl (0.02 normal) after addition of MgO, and the excess acid was back-titrated with standard NaOH of approximately the same normality. While this method gave excellent results when rather high levels of NH_4Cl were added to the soil, the addition of very small amounts (2 m.e. or less per 100 grams) necessitated increasing the sample size to 50 grams or more in order to allow recovery of sufficiently large quantities of ammonia for accurate determination. Accordingly, the size of the sample was reduced to 10 grams, and the Nessler method, essentially as outlined by Peech (48), was adopted for determining ammonium. The only modification made in the method was to include gum arabic (5 ml. or less of 10 per cent NH_3-free gum arabic per 100 ml. of the solution finally read in the colorimeter). As a result, no difficulty was encountered due to the presence of calcium and magnesium, even when the method was applied to KCl extracts of calcareous soils. Results are expressed on the oven-dry basis.

pH. pH determinations were made by means of the glass electrode.

Results and Discussion

Experiments concerning the potassium fixation which occurs under moist conditions

Effect of acid extraction on potassium fixation. In 1941, preliminary experiments were conducted using two calcareous Webster soils (25A and 26A), the general purpose being to investigate the nature of potassium fixation under moist conditions. As has been mentioned, this type of fixation occurs rapidly, and equilibrium is established soon after the addition of potassium. The possibility that the presence of free calcium and magnesium carbonates was in some way concerned with the property of "immediate" fixation prompted a study to determine the effect of acid extraction to remove the carbonates upon this type of fixation. Removal of carbonates was accomplished by successive extractions with 50-ml. portions of approximately 0.2 normal acetic acid. Ten-gram samples were placed in Truog centrifuge tubes (100 ml.) and extractions were continued by centrifuging to clarify the suspension until the pH of the filtrate became 3.5 or less. The excess of acid was then removed by washing with alcohol. Standard KCl solution was then added (1.28 m.e. per 100 grams) after which the tubes stood for 48 hours before being extracted

with ammonium acetate. The data in Table 4 show that the treatment with acid practically destroyed the capacity of these soils to fix potassium under moist conditions. It is of further interest that the acid treatment did not appreciably affect the amount of potassium fixed due only to drying. The evidence obtained with soil 25A showed that the reduction in total fixation which occurred on drying as a result of acid extraction was almost the same as the loss in fixation under moist conditions. Thus, untreated soil 25A fixed 1.12 m.e. of potassium per 100 grams when 1.28 m.e. were added and the soil was dried. After acid extraction the amount fixed on drying was 0.42 m.e. per 100 grams. The difference, 0.70 m.e. is of the same order of magnitude as the corresponding reduction in fixation under moist conditions due to acid extraction, i.e., 0.61 m.e. per 100 grams (Table 4).

Volk (59) showed that extraction of acid soils caused a reduction, but not a loss, in the capacity of acid soils to fix potassium on drying. He attributed this reduction in potassium-fixing capacity to dissolution of "alumino-silicate complexes". It is believed that in the present experiment (Table 4), the extraction with acid was controlled to the extent that removal of the carbonates was the principal effect. This treatment is no more drastic than is commonly employed in procedures used to prepare calcareous soils for mechanical analysis. Thus, it appears likely that some other explanation than degradation of the complex involved in fixation must

Table 4 The effect of previous acid extraction of soils upon their capacity to fix potassium under moist conditions.*

Soil	K fixed by untreated soils	K fixed by soils extracted with 0.2 normal acetic acid**
Webster silty clay loam (25A)	0.74	0.13
Webster silty clay loam (26A)	0.78	0.02

* 1.28 milli-equivalents K added per 100 grams of soil. Soil:liquid ratio approximately 1:1. Time of reaction, 48 hours. Results expressed as milli-equivalents per 100 grams of oven-dry soil.

** Extraction was continued until removal of carbonates was complete.

account for the loss in capacity of these soils to fix potassium under moist conditions.

The possibility that hydrogen ions are directly concerned in the effect which acid treatment has on fixation under moist conditions is immediately suggested. Results reported by Martin, et al. (40) lend support to the idea that hydrogen ions become "fixed", thereby effectively reducing the amount of potassium which becomes nonexchangeable. They found that treatment of a calcareous soil with successively higher increments of HCl resulted in a gradual lessening of the capacity to fix potassium under moist conditions, until finally at the highest level of acid, no fixation occurred. These workers, however, offered no specific explanation as to the manner in which hydrogen ions might accomplish this reduction, nor did they consider that a specific type of mineral was concerned.

Acid-solubility of potassium fixed under moist conditions. In order to secure some evidence as to the tenacity with which potassium becomes fixed in moist soil, the solubility in hot dilute acetic acid of potassium fixed under these conditions was studied. Previous to the extraction, the samples had fixed appreciable quantities of potassium during 48 hours of moist storage with KCl solution, and the excess of potassium had been removed in the usual manner by extraction with ammonium acetate. It is seen in the last column of Table 5 that very little of the fixed potassium was removed by the acid. However, the data show that significant amounts of other non-

Table 5 The amounts of non-exchangeable potassium removed by acid extraction.

Soil	Amounts of K fixed under moist conditions*	Total amount of K extracted by hot acetic acid**	Amount of fixed K extracted
	(m.e./100g soil)	(m.e./100g soil)	(m.e./100g soil)
Webster silty clay loam (25A)	0	0.24	
	1.08	0.29	0.05
Webster silty clay loam (26A)	0	0.19	
	1.14	0.25	0.06

* Samples were previously extracted with normal ammonium acetate to remove water-soluble and exchangeable potassium.

** Soils 25A and 26A were extracted with 300 ml. of hot 0.2 normal acetic acid and 150 ml. of hot normal acetic acid, respectively.

exchangeable forms were dissolved.

Fixation with various soil:water rations in relation to the time of contact with KCl solution. In the experiments carried out during 1941, an approximately uniform soil:water ratio was used in experiments dealing with potassium fixation under moist conditions but no particular attempt was made to control this ratio. The possibility that the variable concentrations of potassium which would result from failure to maintain a constant volume of liquid might influence the results led to the following experiment. Several duplicate samples of a calcareous Webster soil (BL1) received uniform additions of KCl and the soil:water ratio was varied as shown in the first column of Table 6. It is evident that not much difference exists between the amounts of potassium fixed after 24 hours at the various ratios. The wider differences evident after 10 minutes appear to be significant since these variations are greater than occurred between duplicate analyses. The reason why the 1:1 ratio favors more rapid fixation during the first 10 minutes is not evident. It appears from the data that the amount of potassium added, rather than the concentration, governed the extent of fixation. It can be seen that with the 1:1, 1:5, and 1:2.5 soil:water ratios, fixation is not much greater at 24 hours than at 10 minutes. Moreover, no further fixation is apparent after 8 days.

Table 6 Fixation of potassium under moist conditions by a Webster soil (BL 1) in relation to the soil:water ratio and the time between addition of K and extraction.

Soil:water ratio	K added (m.e./100g)	K Fixed (m.e./100g soil)		
		10 min.	24 hrs.	8 days
2:1	2.5	0.887	1.035	------
1:1	2.5	1.048	1.079	1.051
1:1.5	2.5	0.941	1.048	------
1:2.5	2.5	0.903	1.018	1.015

Fixation in acid and calcareous soils in relation to the concentration of potassium and time of contact with KCl. Allaway and Pierre (1) showed that acid soils fixed very little or none of the added potassium during a 24-hour period while moist when the amount of potassium added was 252 pounds per acre (0.32 m.e. per 100 grams). However, it was found in the present study that when 1.64 m.e. of potassium were added per 100 grams to several acid soils, measurable fixation occurred under moist conditions. This suggested that concentration of potassium was a factor which should be investigated in acid soils.

Seven neutral to calcareous soils and four acid soils were included in an experiment to further clarify the relation between time of contact and the amount of potassium fixed, and to show the relation between level of potassium applied and the amount of potassium fixed. These results are summarized in Table 7. It is evident that when 0.5 m.e. of potassium was added to the acid soils there was no fixation after 10 minutes, although 0.409 m.e. per 100 grams or 82 per cent of the amount added was fixed by soil BL1 under the same conditions. However, when the rate of application was increased to 2.5 m.e. per 100 grams, measurable fixation occurred within 10 minutes in three of the acid soils.

The data in Table 7 also show that larger amounts of potassium were fixed after 48 hours than after 10 minutes in the acid soils. In general, the percentage increase in fixation which occurred between 10 minutes and 48 hours for acid soils

Table 7. Fixation of potassium under moist conditions by some acid and calcareous soils in relation to the amount of potassium added and the time of contact.*

Soil No.	Soil Type	pH	Exchangeable K	K fixed**(m.e./100g soil)			
				10 minutes		30 min.	48 hrs.
			m.e./100g soil	0.5 m.e. added	2.5 m.e. added	2.5 m.e. added	2.5 m.e. added
37A	Webster silty clay loam	6.9	0.640	--------	--------	0.232	0.463
32AH	Webster silty clay loam	7.3	0.412	--------	--------	0.857	1.040
28A	Webster silty clay loam	7.0	0.711	--------	--------	0.283	0.352
29A	Webster silty clay loam	7.2	0.728	--------	--------	0.521	0.716
34A	Webster silty clay loam	7.3	0.430	--------	--------	0.566	0.759
BL6	Webster silty clay loam	7.2	0.396	--------	--------	0.359	0.721
BL1	Webster silty clay loam	7.5	0.286	0.409	0.903	1.030	1.150
626	Clinton silt loam	5.3	0.270	-0.046	0.143	0.168	0.185
603	Fayette silt loam	5.9	0.277	-0.034	0.048	-------	0.216
BL2	Clarion loam	5.2	0.156	-0.010	0.244	-------	0.443
BL4	Carrington loam	4.8	0.272	-0.043	0.149	-------	0.336

*Soil-liquid ratio - 2.5

was much greater than the percentage increase which occurred between 30 minutes and 48 hours in the Webster soils. Although the comparisons are not strictly valid, there is some indication from these data that equilibrium is attained more rapidly in soils possessing relatively high fixing capacities than in those which fix quite small quantities of potassium. The soil BL1 which possesses the highest capacity for fixing potassium under the conditions maintained, fixed no more potassium after 8 days than after 24 hours (Table 6). In this soil, approximately 90 per cent of the fixation took place within 10 minutes. Martin, et al. (40) studied the rate of potassium fixation in several neutral to calcareous soils of California and found that, under moist conditions, as much potassium was fixed during the first 48 hours as was fixed after 5 years. The speed of the reaction when potassium is added to these calcareous soils is in agreement with the rapid rate at which equilibrium is attained in ordinary base exchange reactions.

Fixation under moist conditions and on drying in relation to the amount of potassium added. An experiment with soil BL1 was carried out in 1946 to determine the amounts of potassium fixed under moist conditions and on drying using several levels of KCl ranging from 0.5 through 10 m.e. per 100 grams of soil. The data are shown in Table 8 and presented graphically in Figure 1. It is apparent that fixation without drying reaches a near-maximum value at relatively low concentrations of added

Table 8. Fixation of K under moist conditions, total fixation on drying, and fixation due only to drying in relation to the amount added to the soil expressed as m.e. per 100 grams.

K added as KCl	K fixed					
	Moist soil (1)		Dried soil (2)		Due to drying only (2-1)	
	m.e.	Per cent of addition	m.e.	Per cent of addition	m.e.	Per cent of addition
			Webster Soil BL1*			
0.5	0.38	76	0.46	92	0.08	16
1.0	0.61	61	0.84	84	0.23	23
2.5	1.07	42.8	1.95	78	0.88	35.2
4.0	1.15	28.8	3.02	75.5	1.87	46.8
6.0	1.20	20	3.93	65.5	2.73	45.5
8.0	1.26	15.8	4.58	57.3	3.32	41.5
10.0	1.29	12.9	4.97	49.7	3.68	36.8
			Webster Soil 25A**			
0.26	0.21	80.8	0.13	50	0	0
0.51	0.31	62	0.34	66.7	0.03	5.9
1.02	0.47	46.1	0.92	90.2	0.45	44.1
2.05	0.74	36.1	1.56	76.1	0.82	40
4.10	0.90	22	2.85	69.1	1.95	47.1
8.20	1.03	12.6	4.2	51.2	3.17	38.7

*Soil BL1: 10 g. samples used. Exchangeable K = 0.33 m.e./100 g.

**Soil 25A: 2 g. samples used. Exchangeable K = 0.44 m.e./100 g.

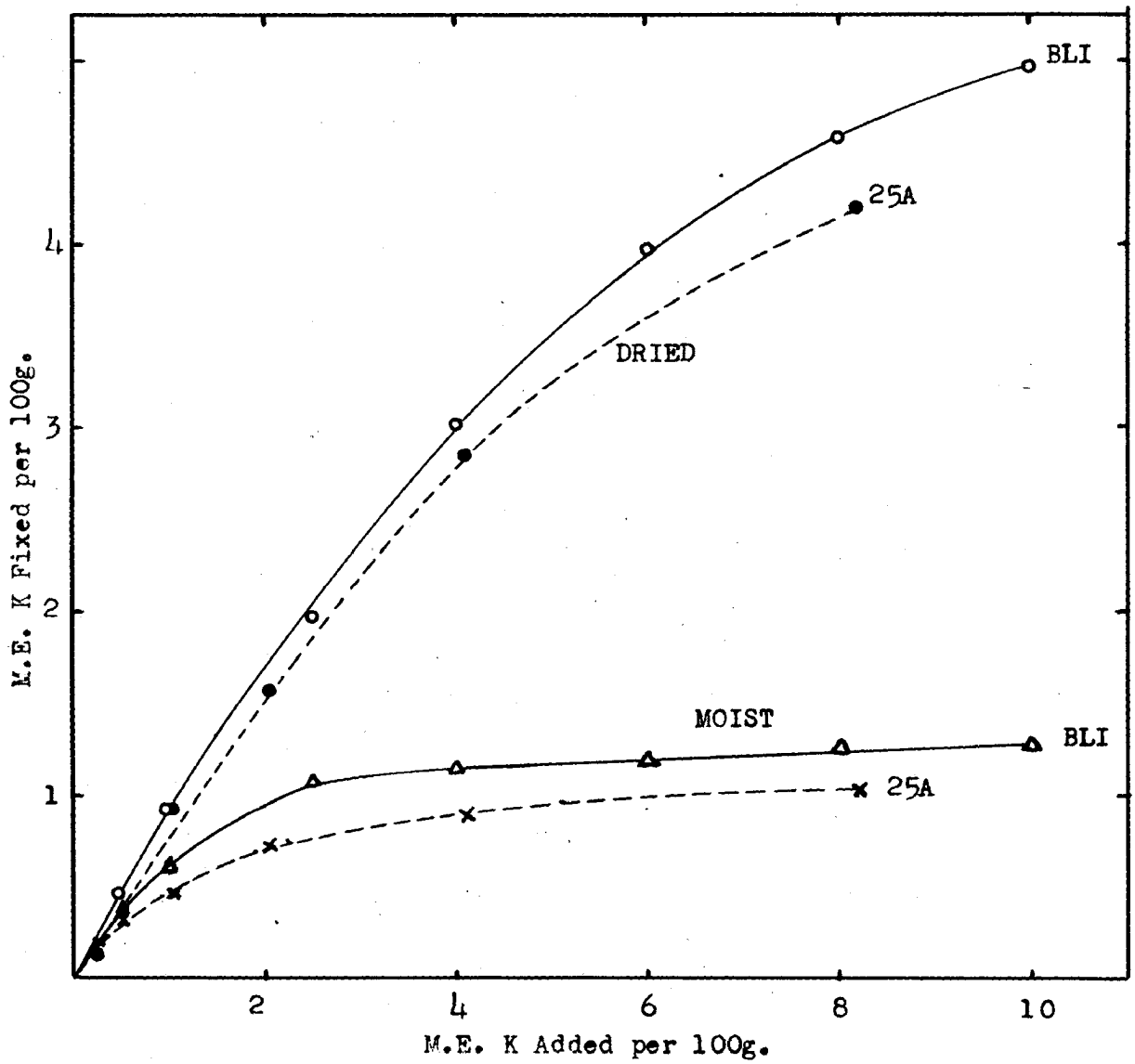

Figure 1. Fixation of K with and without drying by two calcareous Webster soils in relation to the amount of K added.

potassium. There is no indication, however, that the total fixation which occurs on drying at the 10 m.e. level is near the maximum fixing capacity. In Table 8 and Figure 1 the results of a similar experiment conducted in 1941 also are shown. As in the experiment just preceding, it appears that the capacity to fix potassium under moist conditions is definitely limited.

From a study quite similar to those discussed above, Martin et al. (40) concluded that "the increased fixation of potassium in nonreplaceable form on drying the soil may be attributable either to the loss of water or to increase in salt concentration in the liquid phase during the drying process, or to both factors". This, however, does not explain why the lower curves of Figure 1 show no tendency to continue upward even at the higher concentrations of potassium added. In an experiment concerning fixation of ammonium, it was found that no more ammonium was fixed under moist conditions when 2500 m.e. per 100 grams were added than when 10 m.e. were added. Undoubtedly, the soil is in contact with a saturated solution of the salt after considerable amounts of water are expelled during the drying process. Yet, if concentration were the only factor which determined the amount of fixation which occurs, it would seem quite logical that much more fixation should occur when 2500 m.e. of ammonium are added than when 10 m.e. are added.

Relation of Potassium Fixation to Ammonium Fixation in Soils

Evidence that ammonium is fixed in soils. In an experiment conducted in 1941, an attempt was made to determine the effect of various degrees of acid extraction upon the capacity of soil 25A to fix potassium. Following the acid extraction all samples, including the ones which served as controls, i.e., received no acid treatment, were leached with ammonium acetate to remove the exchangeable potassium. It was found upon adding a uniform level of potassium to the ammonium-saturated samples that the capacity to fix potassium under moist conditions had been completely destroyed in every case.

Data showing this effect of extracting with ammonium acetate on fixation of potassium by two soils are given in Table 9. It is significant that resaturating the ammonium-extracted soil 25A with calcium did not restore the capacity to fix potassium under moist conditions. On the basis of this indirect evidence, it appeared likely that ammonium ions were fixed in the same nonexchangeable positions which, in the absence of ammonium, were assumed by potassium ions. Evidence that ammonium actually was fixed in a non exchangeable form was obtained when it was found by direct determination that soil 25A fixed an appreciable quantity of ammonium added as NH_4Cl. This is not the first time that ammonium fixation has been noted in soils. Generally, however, little significance has been attached to the few studies, rather narrow in scope, which have dealt with

Table 9 The effect of extracting two calcareous soils with NH_4-acetate upon the fixation of K under moist conditions (48 hrs.).

Soil	Treatment prior to adding K	Exchangeable K (m.e./100g soil)	K Added (m.e./100g soil)	K Fixed (m.e./100g soil)
25A	None	0.44	2.12	1.08
Webster silty clay loam	Leached with NH_4 acetate	0	2.12	0.02
	Leached with NH_4* acetate	0	2.12	-0.05
26A	None	0.53	2.12	1.14
Webster silty clay loam	Leached with NH_4 acetate	0	2.12	-0.06

*Samples resaturated with Ca following leaching with ammonium acetate.

fixation of this cation. As early as 1917, McBeth (42) reported that he was unable to recover more than 81 per cent of the ammonium salt added to a California soil even after prolonged extraction with 10 per cent HCl. Other evidence which indicates that certain soils may possess the ability to fix ammonium is reported in investigations of methods for determining exchangeable ammonium in soils (5, 41, 44). It was then believed that a suitable method for exchangeable ammonium should allow complete recovery of added ammonium salt. An example is the method of Olsen (44) already cited.

In 1936, Chaminade and Drouineau (11) presented evidence that nonexchangeable ammonium accumulated in soils which had received several applications of ammonium fertilizer over a period of years. They found that more ammonium nitrogen was released from a fertilized soil than from the corresponding unfertilized soil during prolonged grinding in a ball mill. In a later study, Chaminade (9) presented further evidence of ammonium accumulation in a soil as a result of fixation, and reported that this cation fixed by the clay fraction of soils could be liberated by ball-milling or treatment with hydrofluoric acid. These workers measured fixation after the soil or soil colloid had been in contact with a salt solution for a perio d of 2 weeks. Joffe and Levine (29) found that a hydrogen-saturated bentonite and a Montalto colloid fixed appreciable quantities of applied ammonium upon drying.

Certain workers (11,29,45) have concluded that a similar mechanism is responsible for potassium and ammonium fixation. However, there is little quantitative evidence in support of such a theory. The observations that materials which fix potassium likewise are capable of fixing ammonium provide only indirect evidence that the cations assume identical nonexchangeable positions in lattice systems. The primary objective of the experiments to follow was to determine quantitatively the relationship between the fixation of potassium and ammonium, with a view toward establishing whether or not these cations are rendered nonexchangeable through the same mechanism.

Fixation of ammonium and potassium by several soils. The Webster soils which lost the capacity to fix potassium as a result of extraction with ammonium acetate also were found capable of fixing ammonium ions. This indirect evidence indicated that a relationship might exist between the amounts of potassium and ammonium fixed by different soils possessing different fixing capacities. To obtain preliminary evidence on this question, ammonium fixation and potassium fixation were determined separately on 8 soils after a 30-minute period of contact between the salt solution and soil at a soil:water ratio of 1:2.5. A uniform addition of the cation (2.5 m.e. per 100 grams) was made to a 10-gram sample series. The amounts of naturally occurring exchangeable potassium and ammonium were quite variable in these soils from different sites. Thus, the amounts available for fixation, following the addition

of salt solution, were not quite the same for all soils. The data presented in Table 10 and in Figure 2 show, however, that a significant relationship does exist between the capacities of these soils to fix potassium and ammonium.

Effect of ammonium fixation on subsequent potassium fixation. Proof that an identical mechanism is operative in fixation of potassium and ammonium requires the establishment of a fundamental principal, namely, that fixation of either of these ions results in an equivalent reduction in fixation of the other cation. The ensuing experiments were designed for the purpose of determining if such a reciprocal relationship actually exists between potassium and ammonium fixation. Two calcareous Webster soils, possessing relatively high fixing capacities, were employed in these studies.

First of all, ammonium fixation was determined after 24-hour contact on one series of samples which had received ammonium chloride additions of 0, 2, 6, and 12 m.e. per 100 grams of soil. To a parallel series which had previously received the same levels of ammonium, 6 m.e. of potassium per 100 grams were added. The amounts of potassium fixed after moist contact for 24 hours were determined. The results obtained in this experiment and presented in Table 11 show that there is an equivalent reduction in the amount of potassium fixed for each level of ammonium previously fixed. This is evident from the data in the last column which show that the sums of potassium and ammonium fixation are nearly constant. It is quite

Table 10 K fixation and NH_4 fixation under moist conditions in several soils.

Soil No.	pH	NH_4 Fixation (m.e./100g. soil) Exch. NH_4	NH_4 Added	NH_4 Fixed (30 minutes)	K Fixation (m.e./100g. soil) Exch. K	K Added	K Fixed (30 min.)
37A	6.9	0.25	2.5	0.364	0.640	2.5	0.232
34A	7.3	0.19	2.5	0.355	0.430	2.5	0.566
28A	7.0	0.26	2.5	0.296	0.711	2.5	0.283
32AH	7.3	0.14	2.5	0.679	0.412	2.5	0.857
29A	7.2	0.17	2.5	0.307	0.728	2.5	0.521
BL1	7.5	0.07	2.5	0.740	0.286	2.5	1.03
BL6	7.2	0.11	2.5	0.444	0.396	2.5	0.359
626	5.3	0.16	2.5	0.161	0.270	2.5	0.168

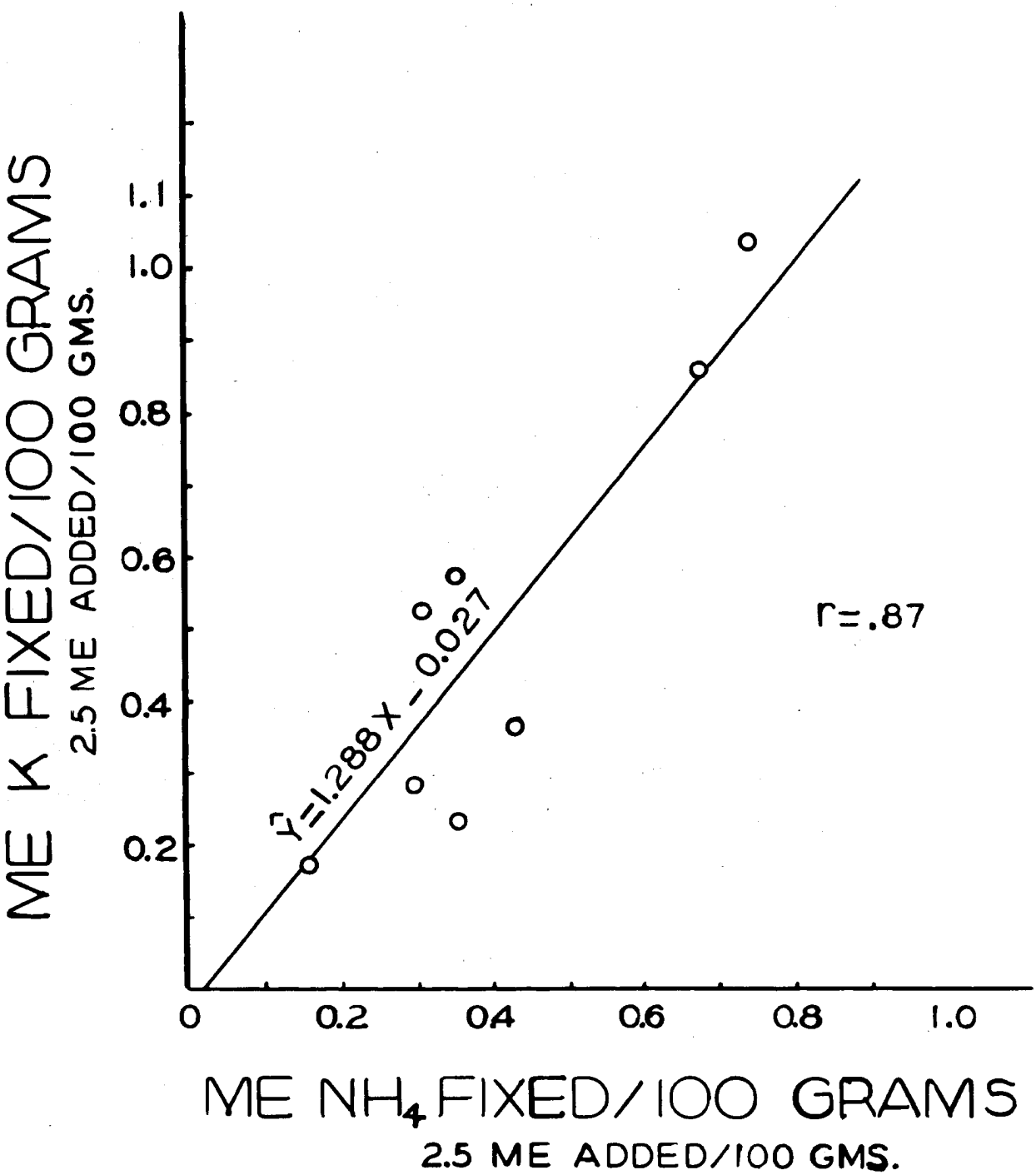

Figure 2. K fixation and NH_4 fixation under moist conditions in several soils.

Table 11 The effect of different levels of non-exchangeable ammonium on subsequent potassium fixation under moist conditions by Webster silty clay loam (25A).

NH_4 added (m.e./100g. soil)	NH_4 previously fixed under moist conditions (m.e./100g. soil)	K fixed following NH_4 additions* (m.e./100g. soil)	Sum: NH_4 K fixed (m.e./100g.soil)
0	0	1.02	1.02
2	0.59	0.41	1.00
6	0.89	0.14	1.03
12	1.14	-0.02	1.12

* Following the period of ammonium fixation (24 hours), these samples each received 6 milli-equivalents of K per 100 grams of soil; soil:water ratio, approximately 1:1.

clear from these values that the capacity of this soil to fix cations is rather definite. This is the first evidence that potassium and ammonium are fixed in the same manner. Under the conditions maintained in this experiment, the capacity for fixation under moist conditions is approximately 1 m.e. per 100 grams of soil. Even when the combined additions of potassium and ammonium reached 24 m.e. per 100 grams, the total fixation was not significantly greater than when 6 m.e. of potassium were supplied alone.

A similar but more comprehensive study was made, using another calcareous Webster silty clay loam (BL1). Two series of soil samples each received increasing levels of ammonium chloride ranging from 0 through 8 m.e. per 100 grams. The soil:water ratio during this initial period was 1:1.5. After one-half hour, ammonium fixation was determined on one of the series. The other series of samples received a constant addition of potassium chloride (2.5 m.e. per 100 grams). After an additional 30 minutes, during which time the soil:water ratio was 1:2.5, potassium fixation was determined on this latter series. From Table 12 and Figure 3, it is evident that, as in the previous experiment, the sums of potassium and ammonium fixation for each level of ammonium fixed are nearly equal and closely approximate the apparent ammonium fixing capacity of this soil.

Effect of potassium fixation on subsequent ammonium fixation. The results from the preceding experiments indicate that increasing the levels of fixed potassium also might bring about

Table 12 The effect of the amount of ammonium previously fixed on subsequent fixation of potassium under moist conditions by Webster silty clay loam (BL 1).

Ammonium Fixation (m.e./100g. soil)		Subsequent K Fixation (m.e./100g. soil)		Sum of NH_4 and K fixed (m.e./100g.soil)
Amount NH_4 added	Amount fixed	Amount added	Amount fixed	
0	0	2.5	1.03	1.03
0.5	0.30	2.5	0.61	0.91
1	0.50	2.5	0.40	0.90
2.5	0.74	2.5	0.26	1.00
4	0.83	2.5	0.15	0.98
5	0.87	2.5	0.14	1.01
6	0.89	2.5	0.10	0.99
8	0.95	2.5	0	0.95
10	0.97	2.5	----	----
12	1.03	2.5	----	----
15	1.03	2.5	----	----

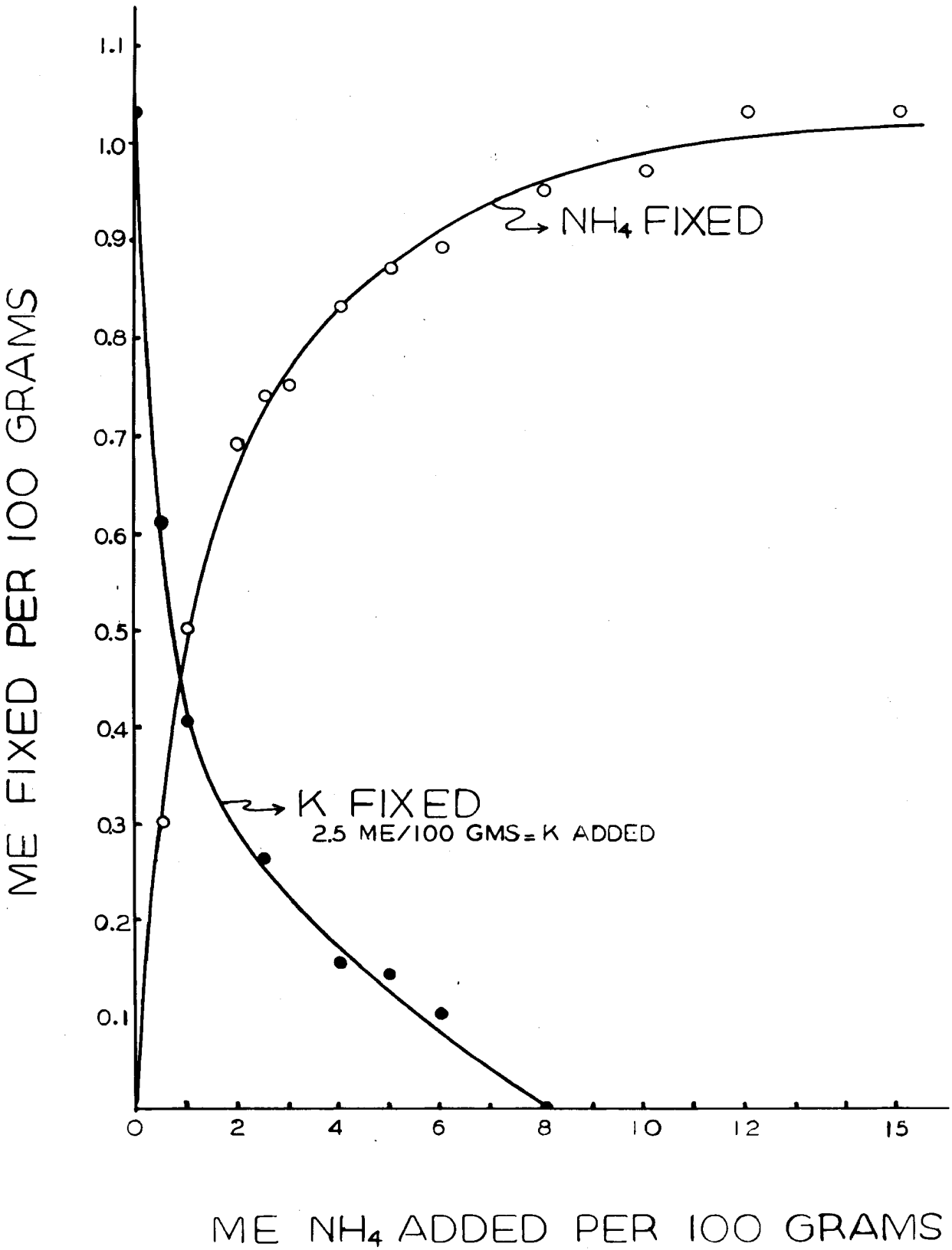

Figure 3. The effect of the amount of NH_4 previously fixed upon subsequent fixation under moist conditions of K.

corresponding reductions in the amounts of ammonium fixed following subsequent additions of the latter cation. In the absence of direct evidence, however, it seemed desirable to investigate this rather important point. Accordingly, two identical series were prepared by adding increasing levels of potassium to 10-gram samples. Potassium fixation was determined after one-half hour on one series. Each sample of the remaining series received 2.5 m.e. of ammonium per 100 grams, and the amounts of ammonium fixed were determined following another 30-minute period of contact. Soil:water ratios employed were the same as in the preceding experiment. The results shown in Table 13 which apply here are presented along with related data shown in the last column which will be discussed shortly. The data are presented graphically in Figure 4. It is clear from the contrasting curves that ammonium fixation is reduced by prior fixation of potassium in the nonexchangeable form. However, an equivalent reduction of ammonium fixation as a result of previous potassium fixation could not be demonstrated in this case. This can be attributed to the fact that the amounts of potassium fixed soon exceeded the ammonium fixation attainable under these conditions, when only 2.5 m.e. of ammonium were added per 100 grams of soil.

In an attempt to demonstrate more conclusively that an increase in the level of potassium fixed is accompanied by an equivalent reduction in the amount of ammonium fixed, another experiment was carried out, this time employing a higher level of ammonium. The experiment differed from the preceding one

Table 13. The effect of the amount of K previously fixed upon subsequent fixation without drying of NH_4 added at the rate of 2.5 m.e. per 100g. of soil.

K Fixation (m.e./100g. soil)		Subsequent NH_4 fixation (m.e./100g.soil)		
K* Added	K Fixed (30 min.)	NH_4 Added	NH_4 Fixed (30 min.)	
			Excess K present	Excess K** removed
0	0	2.5	0.74	0.76
0.5	0.51	2.5	0.43	0.37
1.0	0.67	2.5	0.26	0.20
1.25	----	2.5	0.19	----
1.5	----	2.5	0.15	----
2.0	----	2.5	0.12	----
2.5	1.03	2.5	0.06	0.03
3	----	2.5	0.04	----
4	1.11	2.5	0.06	0.02

*The K fixation at all levels of added K was not determined, since this was not believed necessary for the objective of the experiment.

**After the 30-minute period of contact between K and the soil, excess K was removed by extraction with Ca-acetate (1 normal). Excess Ca was removed with water and 2.5 m.e. of NH_4 were added per 100g. of soil.

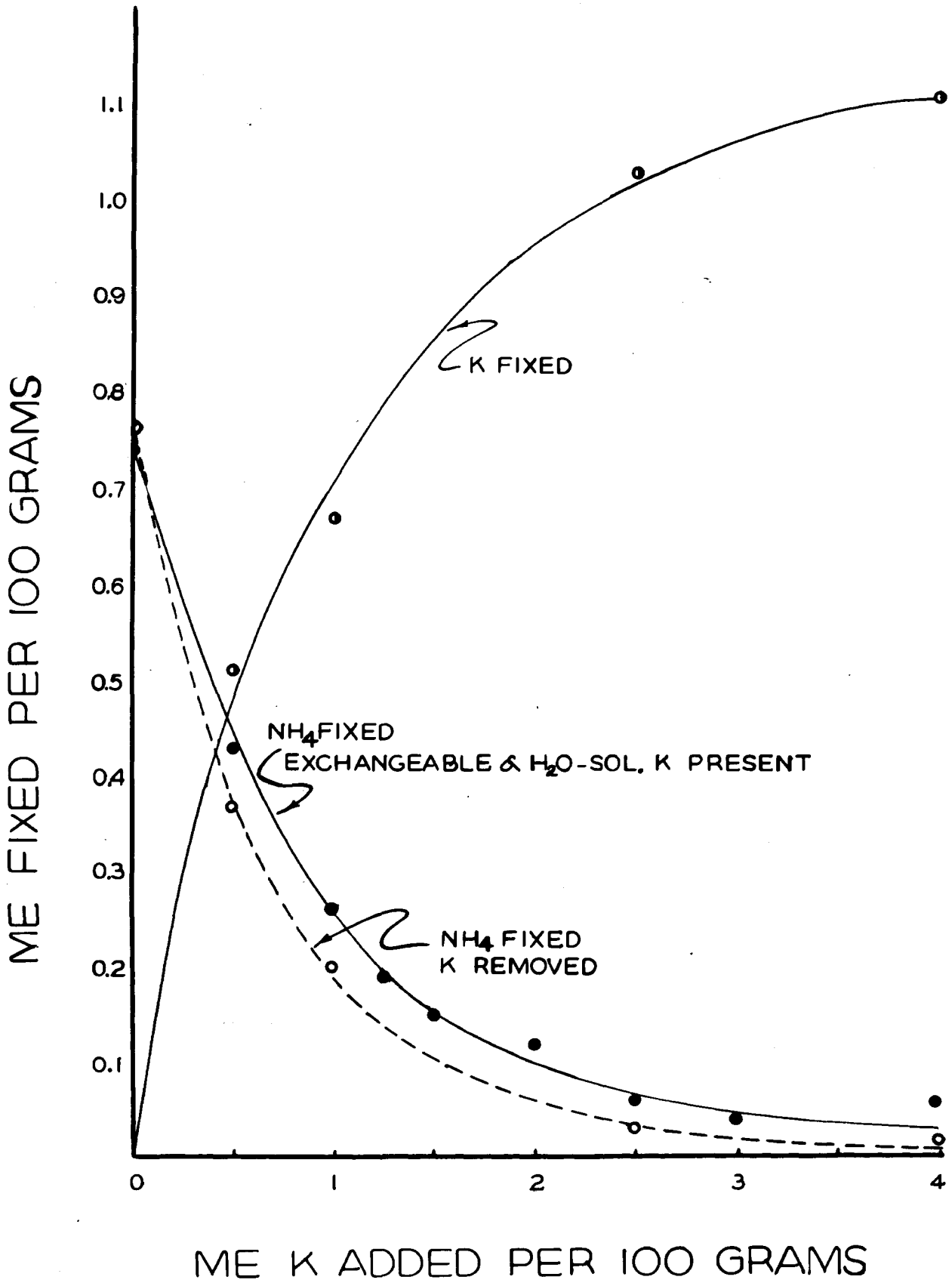

Figure 4. The effect of the amount of K previously fixed upon the subsequent fixation under moist conditions of NH_4 by soil BL1.

only in the addition of 10, instead of 2.5 m.e. of ammonium per 100 grams of soil, following the period of potassium fixation. The potassium-ammonium relationships, already noted in the previous experiment, also are illustrated by the curves in Figure 5. The data are tabulated in Table 14. The application of 10 milliequivalents of ammonium per 100 grams still was not great enough to bring the total fixation of potassium and ammonium as high as the potassium fixation which took place upon the addition of 6 or 10 milliequivalents of potassium applied alone. For this reason, fixation at the two higher levels of potassium may be disregarded in a consideration of the reduction in ammonium fixation due to potassium fixation. The total fixation of these cations for the levels 0, 0.5, 1, 2.5, and 4 m.e. of potassium per 100 grams were 0.97, 1,11, 1.00, 1.15, and 1.14, respectively. These results provide proof that increasing the level of potassium fixed is accompanied by an equivalent reduction in the amount of ammonium fixed.

The question might be raised as to whether the reduction in fixation of potassium or ammonium is due entirely to the filling of nonexchangeable positions by the ion first introduced. It appeared that the presence of appreciable quantities of water-soluble and exchangeable cations might, in itself, be a factor contributing to the reduced fixation of the ion subsequently added. Accordingly, the experiment which has been discussed and presented in Figure 4 and Table

Table 14 The effect of the amount of K previously fixed upon subsequent fixation under moist conditions of NH_4 added at the rate of 10 m.e./100g. soil.

K Fixation (m.e./100g.soil)		Subsequent NH_4 Fixation (m.e./100g.soil)		Sum of NH_4 and K Fixed (m.e./100g soil)
K Added	K Fixed (30 min.)	NH_4 Added	NH_4 Fixed (30 min.)	
0	0	10	0.95	0.95
0.5	0.51	10	0.60	1.11
1.0	0.67	10	0.33	1.00
2.5	1.03	10	0.12	1.15
4	1.11	10	0.03	1.14
5	1.17	--	----	----
6	1.15	10	0.06	1.21
10	1.32	10	0.01	1.32
15	1.29	--	----	----

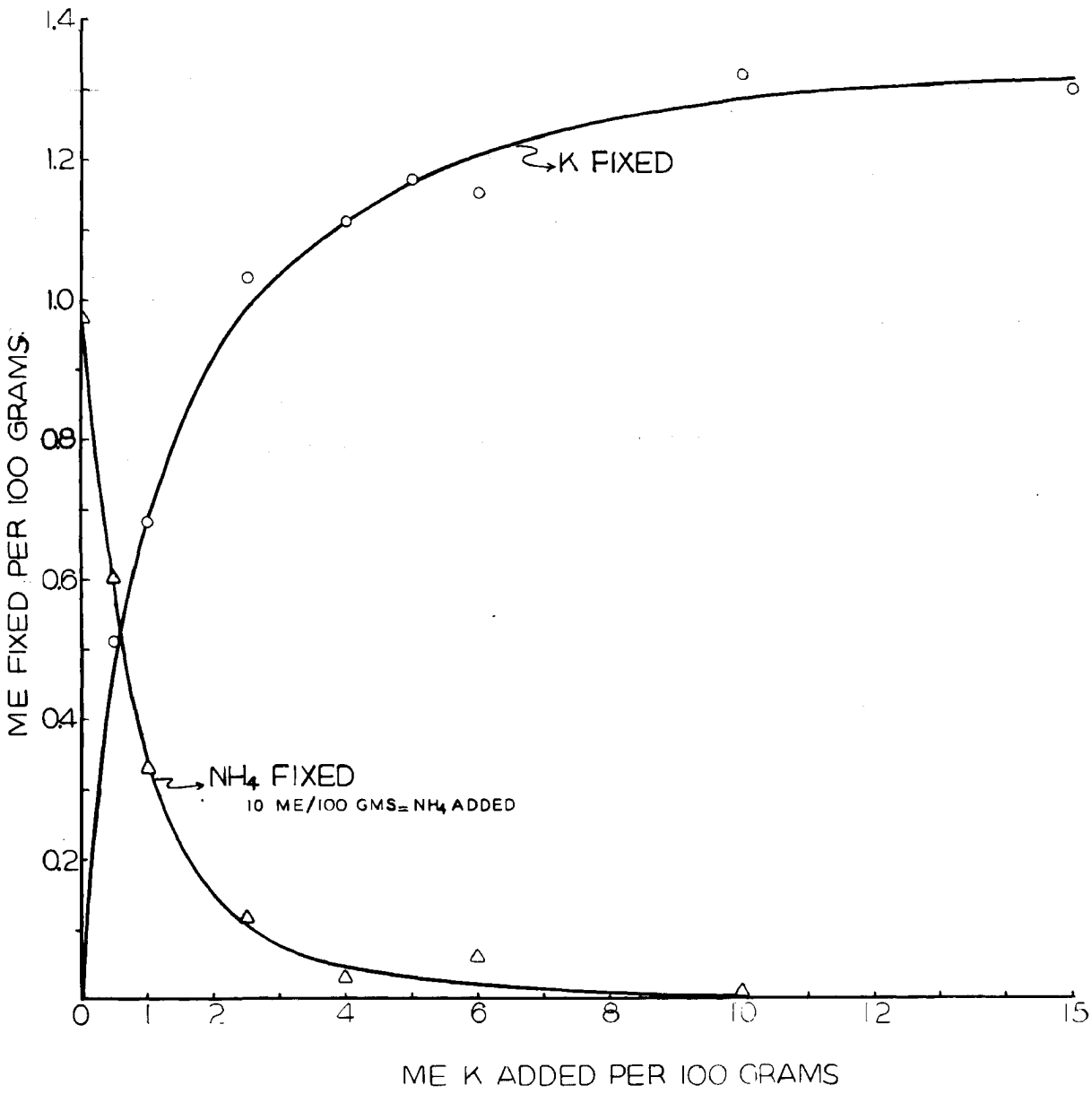

Fig. 5. The effect of the amount of K previously fixed upon subsequent fixation under moist conditions of NH_4.

13 was repeated in the same manner except that, following the period of potassium fixation, water-soluble and exchangeable potassium were leached out with 300 ml. of normal calcium acetate. The soil then was leached extensively with distilled water, leaving calcium-saturated samples. These received ammonium chloride at the rate of 2.5 m.e. per 100 grams, and the amount of ammonium fixed was determined after 30 minutes. The amounts of ammonium fixed are shown in the last column of Table 13. The similarity between the two lower curves of Figure 4 indicates that the presence of considerable amounts of exchangeable and water-soluble potassium was not an important factor influencing the subsequent fixation of ammonium. Thus, it appears that reversion of potassium to the non-exchangeable form, per se, is responsible for the reduction and, ultimately, the loss in ability of this soil to fix ammonium.

Effect of extracting a soil with ammonium acetate upon the fixation of potassium due to drying. Evidence that potassium and ammonium are fixed in identical nonexchangeable positions in moist calcareous Webster soils suggested another approach to the problem of determining whether the type of fixation which occurs under moist conditions is distinct from that which occurs on drying. It was conjectured that once the positions concerned in "moist fixation" became filled with ammonium ions, the positions which fix potassium only when the soil is dried should still be capable of functioning in potassium fixation.

Twelve 10-gram samples of soil BL1 were extracted with ammonium acetate in the usual manner. After standing saturated with this reagent for 48 hours, the samples were leached with calcium acetate to remove all of the exchangeable ammonium. The excess of calcium was then removed by leaching with water, and the samples were transferred to flasks. Another series of samples which had previously fixed potassium without drying as shown in column 3 of Table 15 also were leached with ammonium acetate and were saturated with calcium in the manner described above. Both series of Ca-saturated samples received the six levels of potassium shown in columns 5 and 7 of Table 15, which are equivalent to the amounts of potassium remaining in solution and in exchangeable form after fixation under moist conditions had taken place (see Column 3). The samples, after receiving potassium, were alternately wetted and dried five times at 95 degrees C. The amounts of potassium fixed due to drying only, following removal of the capacity to fix potassium under moist conditions by extraction with ammonium acetate, are recorded in columns 6 and 8 of Table 15. The calculated values showing fixation due only to drying in the untreated soil are shown in column 4. The agreement between calculated and determined values for fixation due only to drying is quite close.

Solubility in acid of the ammonium fixed under moist conditions. That the nonexchangeable ammonium fixed under moist conditions is quite insoluble in normal acetic acid is

Table 15. Evidence that leaching with NH_4-acetate destroys the capacity of soil BL1 to fix K under moist conditions without affecting the capacity to fix K on drying. (Expressed as m.e. per 100 grams.)

Untreated soil			Soil leached with NH_4-acetate and saturated with Ca prior to addition of K		K previously fixed without drying (Col. 3); soil leached with NH_4-acetate and saturated with Ca prior to addition of K	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
K added as KCl	Total fixation on drying	Fixation without drying	Fixation due only to drying	K added as KCl*	Fixation due only to drying	K added as KCl*	Fixation due only to drying
0.5	0.46	0.38	0.08	0.43	0.03	0.43	0.07
1.0	0.84	0.61	0.23	0.72	0.13	0.72	0.16
2.5	1.95	1.07	0.88	1.77	0.98	1.77	0.77
4.0	3.02	1.15	1.87	3.18	1.78	3.18	1.85
6.0	3.93	1.20	2.73	5.13	2.55	5.13	2.73
10.0	4.97	1.29	3.68	9.05	3.10	9.05	3.53

*These values are equivalent to the amounts of K remaining in exchangeable and water-soluble form after the fixation shown in column 3 had occurred following additions of K shown in column 1.

made evident from the results shown in Table 16. The samples used in this study had previously fixed ammonium (see Table 13) and all of the water-soluble and exchangeable ammonium had been removed by extraction with KCl. It can be seen that considerable amounts of ammonium were extracted, but no more came from the samples which had fixed ammonium than from those which had fixed little or none. Most of the extracted ammonium probably came from the organic matter.

These results suggest that Olsen's method (44) for determining exchangeable ammonium may be more empirical than previously has been supposed. Furthermore, it is possible that the recovery of ammonium added to certain soils by extracting with HCl-KCl solution may be more apparent than real. Certainly the ammonium extracted in this manner is not all exchangeable as ordinarily defined.

Table 16 Recovery of nonexchangeable NH_4 from soil BL1 by extraction with normal acetic acid.*

NH_4 previously fixed under moist conditions (m.e./100g. soil)	Total NH_4 recovered (m.e./100g. soil)	Fixed NH_4 recovered (m.e./100g. soil)
0.95	1.58	0.01
0.60	1.50	-0.07
0.33	1.70	0.13
0.05	1.57**	----

* 10g samples were digested for 12 hrs. with hot 1N acetic acid and then were leached on Buchner funnels with an additional 100 ml. of warm acetic acid.

** 1.57 m.e. subtracted from other values to give values of last column.

THE FIXATION OF POTASSIUM UNDER MOIST CONDITIONS AND ON DRYING IN RELATION TO THE TYPE OF CLAY MINERAL

In order to approach in a more definite manner the problem of determining the nature of potassium fixation which takes place under moist conditions, it seemed logical to investigate the clay mineral types which seemed most likely to be concerned. The two clays, illite and montmorillonite, occurring in the calcareous Webster soils and other soils of Iowa (51) were selected for this purpose. The primary objective was to clarify the mechanism responsible for the fixation of potassium under moist conditions, with particular reference to the type which occurs rapidly in certain calcareous soils. The effects of various treatments on the amount of potassium fixed under moist conditions by these clays were determined in order to learn which type of mineral is concerned and the conditions which repress or facilitate the process. Fixation of the potassium on drying also was investigated with each of these clays, using various treatments, with a view toward clarifying the factors which are concerned in this type of fixation in soils.

Materials and Methods

Clay minerals

Preparation of illite clay. The fraction finer than 2μ was separated from "Grundite" supplied by the Illinois Clay Products Company, Urbana, Illinois. The 2μ fraction was washed with dilute HCl (approximately 0.05 normal) by placing the suspension in auto-irrigator pots and removing successive portions of the acid by applying suction. When the leachate no longer gave a test for calcium, the clay was washed free of chloride ions by repeated washings with distilled water. The clay was then dried and ground for a few hours in a ball mill. Unfortunately, the grinding caused appreciable release of nonexchangeable potassium as evidenced by the change in pH from slightly less than 4.0 to 4.4. Moreover, the acid-washed, ground clay contained 6.35 m.e. of exchangeable potassium per 100 grams after grinding. Approximately 400 grams of the acid-washed clay were electrodialyzed for one week. At the end of this period the pH of the clay was 3.8 and the exchangeable potassium content was 1.77 m.e. per 100 grams. This time the clay was not dried, but was suspended in a suitable volume of distilled water. Aliquots were taken with a pipette and dried as a means of determining the concentration of the clay suspension. In all studies with this clay, the suspension was employed.

A few experiments were carried out using the stock of acid-washed illite clay mentioned above from which the electrodialyzed clay was prepared. A suspension was made and its concentration of clay was determined.

Preparation of bentonite clay. Wyoming bentonite (Volclay) from the American Colloid Company, Chicago, Illinois, was acid-washed before fractionation in the manner described above for illite. The coarse material (approximately 5μ and less in diameter) was removed by sedimentation and the finer material was reserved for experimentation. The pH of the hydrogen bentonite suspension was 3.8. Addition of KCl lowered the pH to 3.2. The concentration of the suspension of clay was then determined.

Chemical methods

Potassium fixation. The clay suspensions were shaken well before each aliquot was taken. Usually 25 ml. of the suspension were transferred to an Erlenmeyer flask. This volume of the suspension represented 3.66 grams and 1.56 grams (oven-dry) of illite and bentonite, respectively. In certain experiments 10 ml. of the illite suspension were used. The amounts of potassium salt and/or reagents then added varied with the type of experiment and are designated in presenting the results of the experiments. Fixation under moist conditions took place in the suspension after the additions were made. The flasks were stoppered and allowed to stand

for 48 hours. Then 100 ml. of normal ammonium acetate (pH 6.8) were added and the suspension was shaken for two hours in an end-over-end shaker. After filtering through Buchner funnels using suction, several portions of the extractant were slowly leached through the clay under gentle pressure until the total volume of extractant used was 250 ml. Lawton's (35) method was then followed in determining potassium on the leachate.

The method for determining fixation under moist conditions in the soils was the same as has been described previously.

In determining fixation by clays on drying, the procedure was identical to the one already described for clays, except that the suspensions were dried once in an oven at 100 degrees C. instead of remaining moist. A small amount of distilled water was then added and the samples were allowed to rehydrate for several hours before addition of ammonium acetate and extraction of potassium in the manner previously related.

Adjustment of pH. In some of the experiments to be reported, it was necessary to measure the pH values which had been attained in the suspensions after 48 hours. The glass electrode could not be used in the suspensions which subsequently were to be extracted for determination of potassium, since contamination with potassium from the salt bridge would occur. Therefore, separate series of samples to be used solely for pH measurements were prepared in the same manner

as those used in the determination of fixation. In certain experiments where it was desired to obtain a range of pH values, the first step was to prepare a titration curve showing the relation between the amount of base added to the clay and pH. This curve then provided the means of selecting the range and intervals of pH desired in the study. In most of the studies, standard NaOH was used to adjust the pH of the clay suspensions. In other cases it was necessary to determine pH after addition of various reagents which altered the reaction of the clays.

Determination of aluminum. Aluminum was determined on a series of samples to which fluoride had been added. Fluoride interferes with the precipitation of aluminum by bases, but this interference is obviated by precipitating the aluminum as the 8-hydroxyquinolate in strongly alkaline solution. The procedure followed was based on the methods and principles stated by Kolthoff and Sandell (34). The ammonium acetate extract of the fluoride-treated clay was evaporated to dryness, and organic matter was destroyed by adding 5 ml. of 6 per cent hydrogen peroxide. One ml. of concentrated HCl and 25 ml. of distilled water were added to the residue. The solutions were heated, filtered, and the small silica residue remaining on the filter paper was washed with several portions of hot dilute HCl. Two ml. of 5 per cent 8-hydroxyquinoline in acetic acid were added to each filtrate. After warming the

solution approximately to 70 degrees C., concentrated ammonium hydroxide was added drop-wise with vigorous stirring until the precipitate began to form. Two ml. of concentrated ammonium hydroxide then were added slowly with stirring. After digestion for one hour on the steam chest, the precipitate was collected by filtering through weighed Gooch crucibles fitted with asbestos pads. The precipitates were washed with hot water and dried at 110 degrees C. to constant weight.

Exchange capacity. Exchange capacities of the clays were determined essentially as described by Peech (48), except that ammonium ions were removed from the ammonium-saturated clays by leaching with normal KCl instead of acidified NaCl (10 per cent). No gum arabic was necessary in the colormetric procedure for ammonium since calcium and magnesium were not present.

Results and Discussion

Relation of pH to potassium fixation in clay minerals

Fixation by illite clay adjusted to different pH values with NaOH. When lime is added to certain soils, the capacity to fix potassium increases, while in other soils it has been reported that liming had little or no effect. This problem has been discussed in a comprehensive manner by Peech and Bradfield (49), York and Rogers (66), and others (25). These results, together with the knowledge that certain calcareous

soils possess a high capacity for potassium fixation suggested that some relationship existed between pH and reversion of potassium to nonexchangeable form.

Preliminary work with acid-washed illite showed that more potassium was fixed from KOH than from an equivalent quantity of KCl. On the basis of this evidence an experiment was carried out with electrodialyzed illite to determine in detail the relation between pH and potassium fixation. Aliquots of clay suspension were adjusted to various pH values ranging from 3.8 to 9.8 by adding standard NaOH. A constant level of KCl was added. The results showing reversion of potassium to nonexchangeable forms are presented in Figure 6 and Table 17. The data show that pH changes are accompanied by marked effects on fixation, particularly when the system is dried. The curve which depicts fixation on drying rises uniformly as the pH increases from 3.8 to about 7. Beyond this point, the change in fixation per unit rise in pH is less. There is some indication that the maximum fixation is reached in the vicinity of pH 9. Under moist conditions a gradual increase in fixation is noted until the pH reaches a value between 8 and 9, in which interval the maximum effect associated with pH is attained.

The rather remarkable effects on fixation of potassium which result from raising the pH with NaOH might be explained in two ways. First, NaOH may neutralize and replace hydrogen ions occurring within lattice positions where potassium nor-

Table 17. The fixation of K by electrodialyzed illite clay under moist conditions and on drying as affected by pH.

Percent* Saturation with Na (calculated)	pH** (48 hrs.)	Exchangeable K K added (m.e./100g.soil)	K Fixed (m.e./100g. soil)	
			Moist (48 hrs.)	Dried
0	3.8	8.56	0.57	1.18
15.2	4.4	8.56	0.59	----
38	5.1	8.56	0.79	2.03
45.6	5.5	8.56	0.76	2.13
53.2	5.7	8.56	0.81	2.26
62.2	5.8	8.56	----	2.49
68.4	6.1	8.56	0.79	2.82
83.6	6.8	8.56	0.98	3.16
107	8.3	8.56	1.28	3.61
122	8.9	8.56	1.42	3.96
137	9.7	8.56	1.33	3.94
152	9.8	8.56	1.46	4.18

*Exchange capacity of illite = 33 m.e. per 100 g.
**pH of suspension before drying.

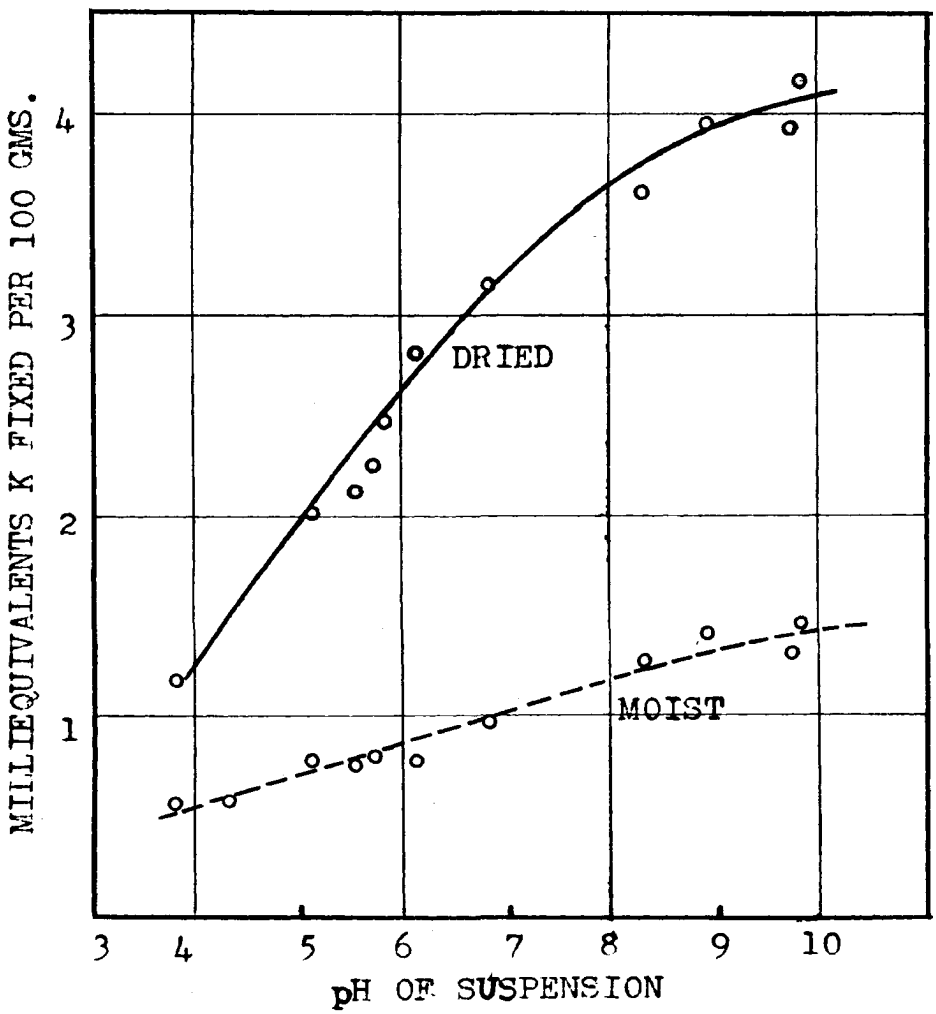

Fig. 6. The fixation of K by electrodialyzed illite clay under moist conditions and on drying as affected by pH.

mally is fixed. This would result in a greater tendency for potassium to resume the positions where fixation occurs, since potassium can more readily replace sodium ions than hydrogen ions. The second possible explanation is based on the assumption that aluminum ions are present in positions once occupied by potassium and that removal of these strongly adsorbed cations likewise acts to promote potassium fixation. The existence of aluminum in certain positions other than fixed lattice positions of the micas is strongly suggested from the work of Paver and Marshall (47) and Schachtschabel (53). The latter worker has shown that various cations, notably hydrogen ions, displace some of the potassium ions situated within the "intramicellar" spaces of micas. Apparently there is no reason why iron and aluminum ions should not take part in such exchange under suitable conditions. Once these cations, by whatever means, have exchanged for potassium in intramicellar positions, it seems likely that the reentrance of potassium may be greatly hindered. Thus, it is possible that NaOH causes increased fixation of potassium in illite by removing aluminum from effective competition with potassium ions, first by precipitation as $Al(OH)_3$ and finally at pH values above the isoelectric point, by formation of $NaAlO_2$. A similar explanation might apply in attempting to account for various results which have been reported showing that extractions of soils and certain minerals with Na_2CO_3 solution caused increases in potassium fixation (40,58,59).

Fixation by bentonite clay adjusted to different pH values with NaOH. Since clay minerals of the montmorillonite group also comprise a significant portion of the clay fraction in many soils, an experiment was conducted in the manner described for illite in order to determine the relationship between pH and the amounts of potassium becoming nonexchangeable. The data in Table 18 not only confirm another observation (45) that montmorillonite fixes little or no potassium when moist, but also show that under moist conditions pH increases do not induce fixation in this mineral. The data showing fixation with and without drying also are presented in Figure 7. It is evident that increasing the pH from 3.2 to 5.9 with NaOH brings about a rather sharp reduction in fixation on drying. However, there is little change in the amounts of potassium fixed between pH 5.9 and 10.6.

The reason for the marked reduction in the amount of potassium rendered nonexchangeable by bentonite following addition of NaOH is not obvious. The various contributing factors might be (1) competition between sodium and potassium for exchange positions; (2) the tendency for bentonite to swell when made alkaline with NaOH (19), thus releasing part of the entrapped potassium; (3) precipitation of aluminum and iron hydroxides between the sheets (47) which in addition to "blocking" exchange positions might prevent the lattice layers from returning to their normal close spacing when dry-

Table 18. Fixation of K by acid-washed bentonite under moist conditions and on drying at different pH values.

Percent* Saturation with Na (calculated)	pH** (48 hrs.)	Exchangeable K K added as KCl (m.e./100g.soil)	K Fixed (m.e./100g. soil) Moist (48 hrs.)	K Fixed (m.e./100g. soil) Dried
0	3.2	17.84	0.23	4.80
8.2	3.8	17.84	0.32	4.57
40.8	5.3	17.84	0.08	3.71
65.4	5.5	17.84	0.05	3.64
81.7	5.9	17.84	-0.20	2.46
94	7.5	17.84	0.05	2.12
98.1	8.5	17.84	-0.20	2.13
102	8.9	17.84	-0.11	2.26
106	9.3	17.84	-0.01	----
147	10.6	17.84	0.05	2.32

*Exchange capacity of bentonite = 72 m.e. per 100g.

**pH of suspension before drying.

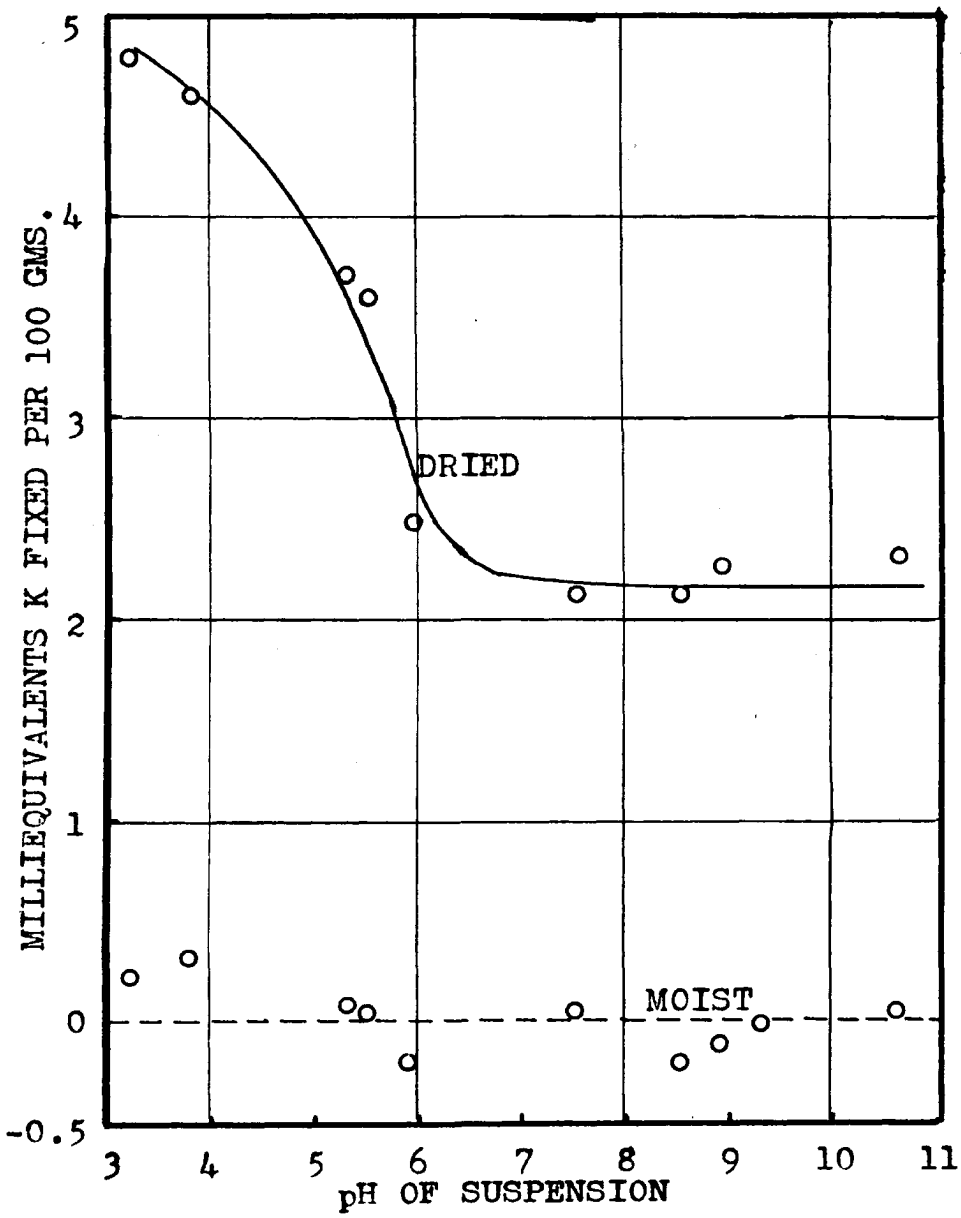

Fig. 7. Fixation of K by acid-washed bentonite under moist conditions and on drying at different pH values.

ing occurs (45). Further work of a more direct nature is needed in order to establish or disprove the validity of the latter theory.

Precipitation of $Al(OH)_3$ between lattice unit sheets may account for the sharp decline in fixation of potassium as the pH rises approximately to seven. Since, as the pH continues to rise the formation of $NaAlO_2$ becomes more pronounced, it is clear that some other reason than precipitation must be advanced to account for the consistently lower amounts of potassium fixed at pH values above seven. It is significant in explaining the low fixation at the higher pH values that the samples represented by the last four points on the upper curves (Figure 7) rehydrated and swelled readily after being rewetted. The apparent volume of the colloidal mass in these clay samples soon became much larger than was evident in the samples receiving lesser quantities of NaOH. These observations are not surprising, since the effect of large amounts of NaOH in causing bentonite clays to swell is common knowledge (19). It appears that the presence of large quantities of NaOH, per se, accounts for the greatly reduced fixation of potassium in the range where $NaAlO_2$ is formed in abundance.

Fixation by bentonite and illite clays as affected by $Ca(OH)_2$ additions. In view of the possible effects which might be attributed directly to sodium, it seemed desirable

to determine if $Ca(OH)_2$ additions caused a similar reduction in fixation by bentonite. Two levels of $Ca(OH)_2$ were added to separate bentonite suspensions using the same level of potassium which was employed in the study with sodium. The samples were dried in the usual manner. The effect of adding this base to illite on fixation under moist conditions also was determined. The results presented in Table 19 show that illite and bentonite clays do not respond alike to this treatment, although the effects are not so marked as when NaOH was added. According to Grim (19), the differential effects of calcium and sodium illustrated in the two experiments with bentonite clay may be due to the fact that much less water is permitted to enter between the sheets when calcium is present than when sodium is present. The divalent ions are considered to resist the entrance of water through bridging action, while sodium ions are quite ineffective in opposing the rehydration and swelling. Among the factors which likely contribute to the reduced fixation by bentonite following addition of $Ca(OH)_2$ are those already mentioned, namely precipitation of hydroxides and possibly calcium-potassium competition (30). Neutralization of hydrogen ions and precipitation of $Al(OH)_3$ probably account for the increased fixation brought about when the pH of illite was raised by adding $Ca(OH)_2$. The fact that the increase is not so great as when NaOH was added is probably

Table 19. The effect of $Ca(OH)_2$ on fixation of K by illite and bentonite clays.

$Ca(OH)_2$ Added***	pH of illite Suspension**	K Fixed* (m.e./100g.)	
		illite	bentonite
0	3.8	0.60	4.86
1 Symmetry	6.6	0.60	3.34
2 Symmetry	8.6	0.97	3.34

* Fixation occurred under moist conditions (48 hrs.) in illite; the bentonite suspension was dried once at 100°C.

** Values shown were measured at 48 hrs.; pH values after 1 week were 6.2 and 7.8 for the 1 S and 2 S levels of $Ca(OH)_2$, respectively.

*** The exchange capacity of the illite and bentonite are 33 and 72 m.e. per 100 g., respectively.

due in part to a slower reaction with the weaker base. This could be ascertained by comparing potassium fixation in the sodium and calcium systems after longer periods of contact.

Effect of phosphate on potassium fixation in clay minerals

Fixation by illite clay as affected by phosphate. The possibility that aluminum might effectively inhibit the entrance of potassium into its normal lattice positions prompted the ensueing studies to determine the influence of phosphate additions on the process of fixation. Wood and DeTurk (63) found that certain soils fixed considerably more potassium when KH_2PO_4 was supplied than when an equivalent amount was added as KCl. Likewise, Wrenshall and Marcello (65) and Joffe and Kolodny (27) found that soils from field plots which had received acid phosphate fixed more potassium than those which were not fertilized.

In an experiment with illite, KH_2PO_4 and KCl were added to separate sets of samples in amounts such that the potassium supplied was equivalent. Fixation of potassium was determined at two pH values, 4.4 and 8.3. At the lower value, $AlPO_4$ is readily precipitated and quite insoluble. At pH 8.3 the solubility of Al^{+3} ions is not a function of phosphate concentration (17). The data in Table 20 show that in the acid clay much greater fixation occurred from KH_2PO_4 than from KCl. However, at the higher pH, potassium fixation was nearly the

Table 20. The amounts of K fixed from KH_2PO_4 and KCl at two pH values by electrodialyzed illite under moist conditions and on drying.

K Salt Added	K Added** (m.e./100g.)	pH of Suspension*	K Fixed (m.e./100g.)	
			Moist	Dried
KCl	6.79	4.40	0.59	1.55
KH_2PO_4	6.69	4.35	1.03	2.94
KCl	6.79	8.30	1.28	3.61
KH_2PO_4	6.69	8.40	1.39	3.53

*Adjusted by adding NaOH.

**Exchangeable K = 1.77 m.e. per 100 g. illite.

same whether phosphate was present or absent. This shows that there was no effect due to phosphate at the pH value where no precipitation of aluminum occurred. Thus, the data strongly suggest that precipitation of iron and aluminum phosphates is concerned directly in the increase in potassium fixation which followed the addition of phosphate. Presumably, iron and aluminum ions are removed from competition with potassium ions as a result of being precipitated as phosphates.

A study of the relation between amount of phosphate added and potassium fixation by illite under moist conditions is presented in Table 21. The data also are shown graphically in Figure 8. The time of contact between clay and added salts was one week. Unfortunately, the pH was not held constant over the entire range of phosphate additions, the difference noted being due to variable additions of Na_2HPO_4. For this reason it is not possible from the experiment to determine the maximum fixation which likely would have been attained at lower pH values within the range of phosphate concentrations employed. It is evident, however, that successively higher increments of the phosphate sharply increased the amounts of K fixed within the pH range 3.8 to 4.6. In this range precipitation of $AlPO_4$ and $FePO_4$ is fairly complete (17). Moreover, the increase in fixation between these pH values cannot be accounted for on the basis of pH alone (Figure 6). At the two highest pH values, which

Table 21. The fixation of K in suspensions of electrodialyzed illite in relation to phosphate concentration and pH.

PO_4 Added (m.e./100g.)	pH	Exchangeable K + K added (m.e./100g.)	K Fixed (1 week) (m.e./100g.
0	3.8	8.56	0.60
20.5	3.8	8.56	1.04
27.4	4.2	8.56	1.60
34.2	4.6	8.56	1.77
47.9	5.4	8.56	1.57
89	6.7	8.56	1.24

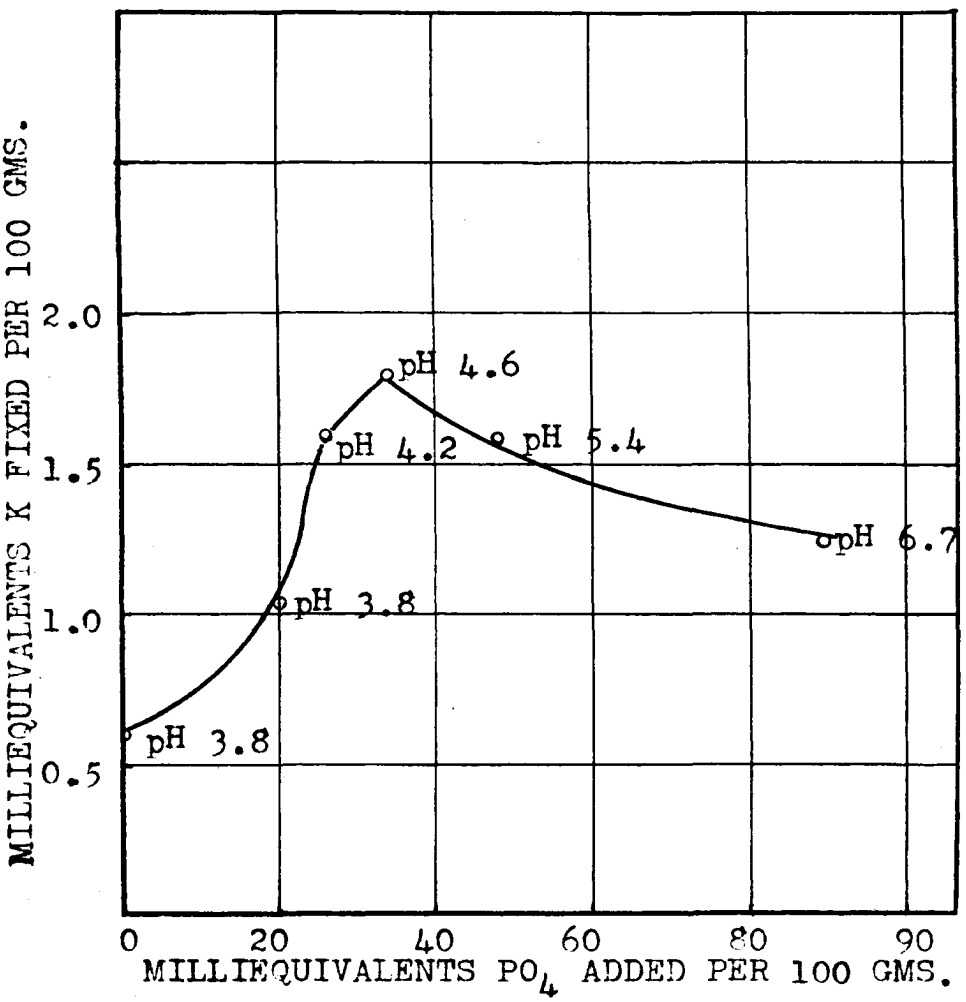

Fig. 8. The fixation of K in suspensions of electrodialyzed illite in relation to phosphate concentration and pH.

correspond to the highest phosphate additions, there is a notable decrease in fixation. On the basis of previous data (Table 20), it may be assumed that further increase in pH would continue to reduce K fixation until the point is reached where no precipitation of phosphate occurs.

Fixation by bentonite clay as affected by phosphate. Addition of phosphate caused a reduction in the amount of K fixed by bentonite on drying. When equivalent quantities of K (17.8 m.e. per 100 grams) as KCl and KH_2PO_4 were added to separate samples of acid-washed bentonite, the amounts of K fixed were 4.8 and 3.9 m.e. per 100 grams, respectively, when the pH was 3.2. In another experiment, 17.8 m.e. of KCl and 64 m.e. of phosphate as Na_2HPO_4 per 100 grams were added to bentonite and the system was dried. The amount of K fixed was 4.06 m.e. per 100 grams (pH 3.3), thus confirming the previous observation that phosphate reduces fixation of K by bentonite. The decrease in fixation which resulted from adding potassium as the phosphate is believed to be due primarily to the precipitation of $AlPO_4$ and much smaller amounts of $FePO_4$ which upon coagulation by heating conceivably might prevent normal closure of the montmorillonite sheets. The results from this experiment corroborate Hoover's (23) finding that the phosphate decreased fixation in a montmorillonitic soil.

Effect of fluoride on potassium fixation by clay minerals

Fixation by illite as affected by fluoride. The previous experiments showing the influence of various additions on fixation of potassium by illite have pointed to the probable importance of aluminum in partially restricting the entrance of potassium into positions where it becomes relatively non-exchangeable. However, the evidence is indirect since the actual release of aluminum from these positions has not been demonstrated by analysis. Since the fluoride ion forms soluble complex anions AlF_6^{-3} and FeF_6^{-3}, this ion was employed in a study with electrodialyzed illite in order to determine its effect on potassium fixation and to provide a means of studying release of aluminum.

Preliminary trials to establish the method for controlling pH in experiments using illite gave the interesting result that electrodialyzed clay could be titrated with the neutral salt, NaF, from pH 3.8 to the pH of the salt (6.9-7). Addition of the other sodium halides, of course, initially lowers the pH of the clay due to replacement of hydrogen ions, and there is little or no tendency for the pH to rise with further additions. In Table 22 is shown the pH values obtained in separate titrations of electrodialyzed illite clay with 0.1 normal NaF and with standard NaOH.

The fact that the pH of the clay is raised by adding successive increments of NaF is strong evidence that electro-

Table 22. The effect of different amounts of NaF and NaOH on the pH of electrodialyzed illite.

NaF added (m.e./100 g.)	pH* (immediate)	NaOH added (m.e./100 g.)	pH (48 hrs.)
0	3.9	0	3.8
		5.0	4.4
8.5	5.1	12.5	5.1
		15.0	5.5
20.5	5.8	17.6	5.7
		20.1	5.8
34.2	6.5	22.6	6.1
		27.6	6.8
41.0	6.7	35.1	8.3
		40.1	8.9
47.8	6.8	45.1	9.7

*These values are within 0.3 pH unit of these which would have been reached at 48 hours.

dialyzing a clay produces an Al-H-Clay rather than an H-Clay. The literature contains numerous references to the fact that "hydrogen-clays" were prepared by acid-washing or electrodialysis. On the other hand, Paver and Marshall (47) present good evidence by another means than that presented in Table 22 that an Al-H-Clay results upon acid-washing or electrodialysis. The results here obtained support their view.

The reactions which occur between NaF and the adsorbed aluminum ions of clay are of interest in connection with any effect which this reagent might exert on potassium fixation. The general reactions which might occur when NaF is added to the clay are presented below. No attempt is made to picture any of the intermediate steps.

The reaction of NaF with exchangeable aluminum might proceed as follows, providing the form of adsorbed aluminum is considered to be $Al(OH)_2^{+1}$, as proposed by Paver and Marshall (47):

$$(1)\quad 6NaF + CLAY\text{-}Al\begin{matrix}OH\\ \rightleftharpoons\\ OH\end{matrix} CLAY\text{-}Na + Na_3AlF_6 + 2NaOH$$

The explanation for the increase in pH of the illite clay upon addition of NaF can be seen in the above equation. If Al^{+3} is the adsorbed form, the following reaction might occur:

$$(2)\quad 6NaF + Al\text{-}CLAY \rightleftharpoons \begin{matrix}Na\\ Na\\ Na\end{matrix}\!\!>\!\!CLAY + Na_3AlF_6$$

Hydrated Fe and Al oxides would also react with NaF according to the following reaction:

$$(3) \quad Al\begin{matrix}OH\\OH\\OH\end{matrix} + 6NaF \rightleftharpoons Na_3AlF_6 + 3NaOH$$

From the equations shown above, it becomes clear why equilibrium is attained rather rapidly. Formation of the complex causes the reaction to proceed rather completely to the right. That the reaction proceeds rapidly is evidenced by the fact that the pH which is determined very soon after addition of the NaF is within 0.2-0.3 pH unit of that found after 48 hours.

In an experiment to determine the effect of fluoride on potassium fixation, two levels of NaF were added to electrodialyzed illite and the amounts of potassium fixed and aluminum released were determined. The weight of each sample was 1.46 grams. The amounts of NaF shown in Table 23 were added and a predetermined quantity of NaOH was added to bring the pH approximately to the desired level. After addition of potassium, the samples stood for 48 hours. They were then extracted with ammonium acetate in the usual manner.

No determinations for iron were made on the clay extract, since it was found by qualitative test that the amount present was insignificant as compared to the relatively large amounts of aluminum extracted. Therefore, a slight error is possible due to the presence of small amounts of iron. The results given in Table 23 show that fluoride ions cause

Table 23. Effect of adding NaF to illite on fixation of K without drying and release of Al.

Fluoride added (m.e./100g.)	pH***	K Fixed* (m.e./100g.)		Al release due to Fluoride (m.e./100g.)**	
		Total	Due to F	Al^{+3}	$Al(OH)_2^{+1}$
0	6.1	0.79	0	0	0
21	6.1	1.67	0.88	3.8	1.3
69	7.0	3.71	2.92	9.1	3.0

* K added + exchangeable K = 8.56 m.e. per 100 g.

** Al^{+3} extracted by NH_4-acetate from sample receiving no F^- = 3.8 m.e. per 100 g.

*** pH adjusted with NaOH, except at highest level of NaF where none was added.

a much greater increase in potassium fixation than has been evidenced by any of the treatments thus far. Based on concepts advanced by Paver and Marshall (47), the form of aluminum removed by complex formation with fluoride ions is considered to be $Al(OH)_2^{+1}$. Calculations on this basis, as shown in the last column of the table, indicate that there is a fairly close agreement between the amounts of potassium fixed and the aluminum released due to fluoride addition. The results cannot be clearly interpreted, however, since the method used does not permit distinguishing between aluminum removed from the outer surfaces and inner surfaces of the clay particles. Nevertheless, there appears to be ample justification, based on a consideration of these data and results presented earlier, to conclude that removal of aluminum, and to a lesser extent iron, from inner positions is responsible for the increase in fixation of potassium.

Another experiment was conducted using acid-washed clay. Aliquots of the suspension containing 3.66 grams of clay were pipetted into flasks. Since the highest levels of NaF used brought the pH to 7 as determined by preliminary titration, there appeared to be no reason for not adjusting all samples to this pH level. Whether or not it is important to control the pH within narrow limits in such an experiment as this one has not been investigated. Evidently such control is not important from the standpoint of complex formation;

however, the solubility of the aluminum silicate (the clay itself) probably varies with the pH, particularly at low and high pH values. Thus, it appeared that a relatively constant pH near neutrality was desirable.

From Table 24 it is evident that fixation of potassium increased as larger amounts of fluoride were added. Due to the presence of an appreciable quantity of exchangeable aluminum in the acid-washed clay (5.1 m.e. per 100 grams), it is not possible to determine how much of the aluminum might have been removed by fluoride from intramicellar spaces of the illite. In light of other evidence, however, a portion of the aluminum released seems definitely concerned with the increase in potassium fixation which accompanies treatment with fluoride.

Fixation by bentonite as affected by fluoride. It appeared from the foregoing studies and from results obtained by Paver and Marshall (47) that acid-washed bentonite also contains exchangeable aluminum adsorbed on the inner accessible surfaces of the clay. The possibility that this was a factor limiting the amount of potassium fixation on drying led to the following study. Duplicate samples (1.56 grams) of the bentonite suspension, each receiving 32 m.e. of NaF and 17.84 m.e. of potassium per 100 grams, were dried once at 100 degrees C. The amount of potassium fixed in these samples was 5.93 m.e. per 100 grams, which is considerably more than was fixed by the samples which received no

Table 24. Effect of adding NaF to acid-washed illite on fixation of K under moist conditions and release of Al. (Expressed as m.e. per 100g.)

NaF Added	K Fixed		Al released* due to F^-	
	Total	Due to F^-	Al^{+3}	$Al(OH)_2^{+1}$
0	0.43	0	0	0
6.8	0.42	0	0.15	0.05
13.7	0.66	0.23	1.94	0.65
20.5	1.54	1.11	2.85	0.95
27.3	1.99	1.56	2.91	0.97

*Al^{+3} extracted by NH_4-acetate with no F^- added = 5.1 m.e. per 100g. The pH of the suspensions was adjusted to approximately neutral with NaOH.

fluoride. The pH after addition of fluoride was 4.2. Samples adjusted to the same pH, but receiving no fluoride, fixed 4.4 m.e. of potassium per 100 grams on drying. These data support the hypothesis that exchangeable aluminum between the sheets of montmorillonite interferes with fixation of potassium.

Effect of oxine and oxalate on potassium fixation by illite and bentonite clays

Illite. Further investigations were carried out using other substances which react with aluminum. The oxalate ion forms soluble complexes with iron and aluminum under suitable conditions (32). The reagent 8-hydroxyquinoline (oxine) precipitates aluminum as Al-quinolate over a wide range of pH values (4.2 to 9.8) (62). These reagents were employed with electrodialyzed illite to determine if fixation in moist clay is affected by their presence. The acetic acid solution of oxine and the oxalic acid solution were adjusted to pH 4.9 using NaOH before being added to the clay. The amounts of potassium fixed under moist conditions (48 hours) in the presence of oxine and oxalate were 0.63 and 0.68 m.e. per 100 grams, respectively. Without these additions 0.70 m.e. was fixed as shown in Table 25. The fact that no increase took place may be explained on the basis that the molecules formed by reaction of alum-

Table 25. Effect of oxine and oxalate on fixation of potassium by illite and bentonite clays.

Clay	KCl added + exch. K (m.e./100 g.)	Treatment*	K fixed (m.e./100 g.)
Illite	8.56	2 ml. 5% oxine + 25 ml. 0.0918 N NaOH; not dried	0.63
	8.56	10 ml. 0.2 N oxalic acid + 35 ml. 0.0918 N NaOH; not dried	0.68
	8.56	pH adjusted with NaOH; not dried	0.70
Bentonite	17.84	2 ml. 5% oxine + 25 ml. 0.0918 N NaOH; dried at 100° C.	4.38
	17.84	10 ml. 0.2 N oxalic acid + 35 ml. 0.0918 N NaOH; dried at 100° C.	2.58
	17.84	pH adjusted with NaOH; dried at 100° C.	4.2

*pH values in these samples ranged from 4.5-5.

inum or iron with oxine and oxalate are known to be quite large (32). It is possible that steric limitations prevent these reagents from reacting with the aluminum inside the intramicellar spaces.

Bentonite. The possibility of gaining further evidence with regard to the importance of spatial limitations through experiments with montmorillonite clay appeared promising, since this mineral possesses an expanding lattice whose flexibility permits the entrance of very large molecules. Accordingly, the effect of oxine and oxalate on fixation of potassium by bentonite was investigated. These results also are shown in Table 25. That the oxalate was able to penetrate between the variable spacings of the clay is evidenced by the reduction in fixation which occurred upon its addition. This marked reduction in fixation resulting from oxalate treatment may be due to the incomplete formation of soluble Al-complex from $Al_2(C_2O_4)_3$ in the acid system (32). The small reduction in potassium fixation which occurred when oxine was added cannot be attributed with definiteness to the formation of Al-quinolate since it is not known whether precipitation actually occurred at the rather low pH value employed (4.6) (62). The latter system requires further study to determine the conditions which are most favorable for precipitation of the aluminum.

Effect of diethylamine-HCl on fixation of potassium by illite and bentonite clays.

Page and Baver (45) found that when diethylamine-HCl was added to a bentonite clay, very little of the added potassium was fixed when the clay was dried. The untreated clay, however, fixed a large amount of potassium. The large organic cation, $(C_2H_5)_2NH_2^+$, was believed to prevent the flexible sheets of montmorillonite from closing, which, according to the theory advanced, would prevent potassium from being fixed. As far as is known, these results have not been confirmed by other workers, although the theory proposed by these investigators appears to have been rather widely accepted.

An experiment was carried out to determine the effect of adding diethylamine-HCl upon the fixation of potassium by illite as well as bentonite. The amount of this reagent added to the clay samples was equivalent to their exchange capacities. The amounts of KCl supplied and other details are given in Table 26. It is seen from this table that fixation of potassium by bentonite was greatly reduced, which is in accordance with the finding of Page and Baver (45). However, there was no significant effect on fixation of potassium by illite on drying. This indicates that the large cation penetrated easily between the sheets of montmorillonite, but remained outside the illite crystal

lattice. The data reemphasize that spatial considerations are involved in comparing the fixation of potassium by these two types of minerals which differ so markedly in their behavior with various treatments.

Fixation by illite clay under moist conditions and on drying in relation to the amount of potassium added

In an earlier experiment (Figure 1), it was shown that the amount of potassium fixed under moist conditions in certain soils reached a near-maximum value which did not change appreciably even when the levels of potassium supplied were quite high. Ion hydration was considered as a possible factor limiting the amount of potassium which could be fixed under moist conditions, since the effective diameters of hydrated ions probably are too great to permit entrance into all of the positions where potassium might be fixed. When the system is dried, however, dehydrated potassium ions may migrate into certain positions which are inaccessible to the hydrated ions and become fixed.

From another experiment shown in Figure 6 it becomes evident that drying facilitates the fixation of potassium by micaceous minerals. In accordance with the previous discussion, it would appear that one of the important factors causing the increased fixation of potassium on drying is the removal of water of hydration, thus increasing the likelihood of these cations becoming nonexchangeable.

Table 26. Fixation of K on drying by bentonite and illite as affected by additions of diethylamine-HCl.

Clay	K fixed (m.e./100 g.)***	
	Amine-HCl* added	No amine-HCl added
Bentonite	0.41	4.86
Illite	1.34**	1.18

*1 symmetry of amine-HCl added

**pH of illite-amine system before drying = 3.9

***Exchangeable K_+ added K : Bentonite = 17.84; illite = 8.56 m.e. per 100 g.

An experiment was conducted to show the relation between the amounts of potassium fixed by illite and the concentration of potassium added. Two series of illite suspensions were adjusted to pH 8.3 by adding NaOH. This was done to minimize the inhibitory effects on fixation of K due to the presence of adsorbed H, Fe, and Al ions. Each series of samples received increasing levels of KCl as shown in Table 27. One set was dried at 100 degrees C. while the other remained moist for 48 hours before extraction with ammonium acetate. The results shown graphically in Figure 9 reveal that the types of curves obtained by plotting fixation versus the amounts of potassium added are quite similar to those which have been obtained for soils (Figure 1).

It is evident that fixation under moist conditions in soils and in illite does not increase beyond a certain amount even when rather high levels of KCl are applied. That ion hydration limits fixation under these conditions again is suggested.

These data strongly indicate that two types of fixation occur in illite - one which takes place under moist conditions and the other on drying. The fixation which occurs in the moist illite probably involves the positions existing at the edges of the crystals, since these spaces conceivably would be the ones most readily accessible to hydrated potassium ions (7,63). The existence of a limited number of such intermicellar positions which have lost K through weathering

Table 27. Fixation of K by electrodialyzed illite in relation to the amount of K added.

K Added* as KCl (m.e./100g.)	pH (48 hrs.)	K Fixed (m.e./100g.) Moist (48 hrs.)	Dried	K Fixed due to drying (m.e./100g.)
1.37	8.3	0.57	0.90	0.33
4.10	8.3	0.82	2.49	1.67
6.79	8.3	1.28	3.61	2.33
13.70	8.3	1.71	5.25	3.54
34.15	8.3	1.71	6.69	4.98

*Exchangeable K = 1.77 m.e. per 100 g.

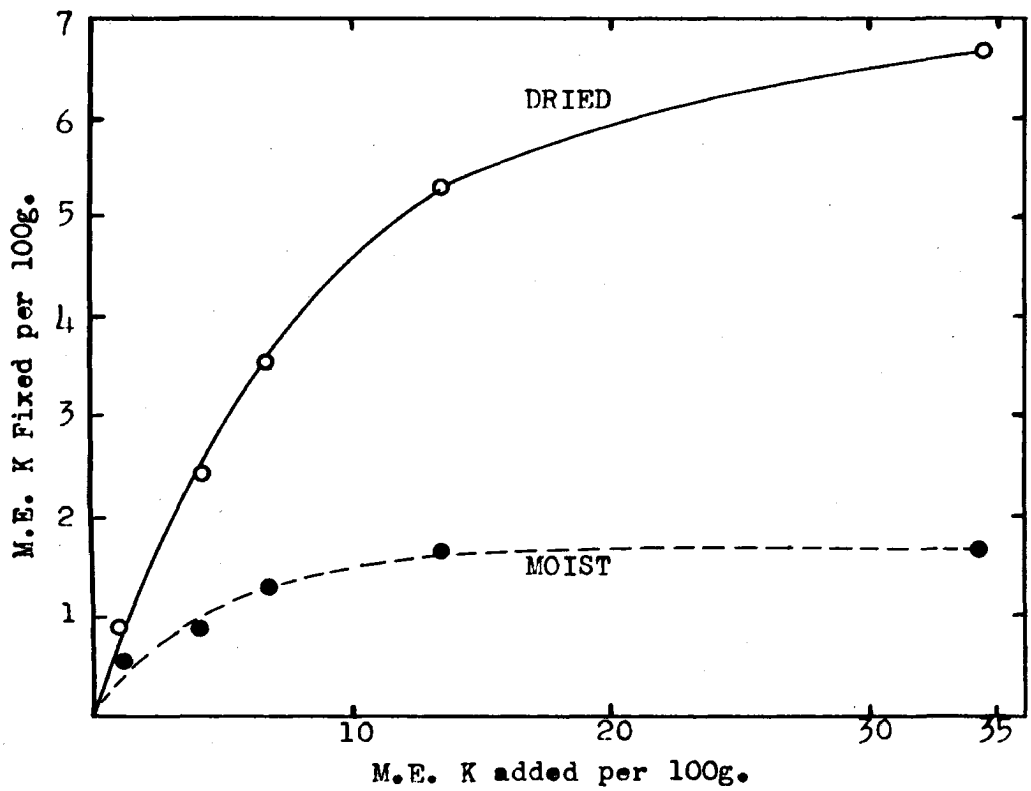

Figure 9. Fixation of K by electrodialyzed illite in relation to the amount of K added (pH 8.3)

would explain why there is a definite capacity for fixation under moist conditions.

When drying occurs, the potassium ions lose the water of hydration, and thus would be capable of penetrating farther into the illite crystal lattice and occupying more deep-seated positions. This theory is supported by results reported by Attoe (2) indicating that there is a distinction between the types of fixation which occur under moist conditions and on drying. This investigator found that the potassium fixed in a moist soil was soluble in 0.5 N HCl, while additional quantities of potassium fixed on air-drying were not dissolved under the same conditions by this reagent. Moreover, Attoe and Truog (3) showed that the soil potassium soluble in 0.5 N HCl is quite readily released to the exchangeable form during cropping, while the acid-soluble portion becomes available to plants much more slowly.

It is recognized that the two "types" of fixation which have been postulated, in reality are concerned with the same kinds of positions. Yet, the distinction made seems justified on the basis of the definite limitations which characterize the fixation of potassium under moist conditions.

GENERAL DISCUSSION

One of the most important objectives of this study was to clarify the mechanism responsible for the conversion of large quantities of added water-soluble potassium salts to the nonexchangeable form in certain soils under moist conditions. In the first phase of the investigation, the capacity to fix potassium under moist conditions was destroyed by treatment of calcareous Webster soils with acid. The results suggested strongly that this effect was due to "fixation" of hydrogen ions in mineral lattice positions which, prior to acid extraction, had been concerned in the "rapid" fixation of potassium. Addition of ammonium salts to these soils also caused a complete loss in the capacity for fixing potassium; the mechanisms of potassium and ammonium fixation were found to be identical.

The role of hydrogen ions in minimizing potassium fixation has been further indicated from results obtained with illite clay. That iron and aluminum have a definite function in restricting fixation of potassium was even more evident. This was established by the very marked effects which phosphate or fluoride additions had upon the fixation of potassium by illite clay. However, in cases where hydrogen ions predominate in the intramicellar spaces, it might be expected that

addition of phosphate or fluoride which react with iron and aluminum but not with hydrogen would have little effect on fixation. In this case, addition of NaOH to neutralize hydrogen ions would bring about increased fixation. An experiment performed with a calcareous Webster soil provided rather clear evidence that this is true. This soil (BL1) fixed a considerable quantity of potassium under moist conditions, but practically lost its capacity to fix potassium under moist conditions when it was treated with acid to the extent that carbonates were neutralized. However, raising the pH with NaOH to near its original value (7.8) partially restored the capacity of soil BL1 to fix potassium under moist conditions. Significantly, phosphate or fluoride had no effect on fixation, which indicated that the comparatively mild acid treatment served to replace calcium, magnesium, and sodium ions with hydrogen ions without bringing measurable quantities of aluminum or iron into solution.

Martin, et al. (40) attempted to restore the capacity for fixation under moist conditions in an acid-washed calcareous soil by resaturating the soil with calcium, using $CaCl_2$, but were unsuccessful. This failure may be explained on the basis of the proposed theory that the hydrogen ions must be neutralized and replaced by a less strongly adsorbed cation such as sodium or calcium before fixation of potassium can again occur under moist conditions to any appreciable extent.

It appears logical from a consideration of certain processes which take place during weathering under either natural or artificial conditions that hydrogen, iron and aluminum ions would tend to replace K ions in the intramicellar spaces of micaceous minerals. During the progressive weathering of micaceous minerals in nature under conditions of acid leaching, there is a slow removal of potassium. Yet the apparent structural configuration of mica is not altered appreciably, even when considerable amounts of potassium have been released through weathering (12). Moreover, Joffe and Levine (28) have shown that practically the same amount of potassium which was released from sericite during electrodialysis could be refixed on drying, thus indicating that little lattice breakdown took place as potassium was removed.

The charge within the clay micelle which would result upon loss of potassium likely is balanced through the introduction of equivalent amounts of other cations by direct exchange. Under weathering conditions which prevail in acid soils, the ions high in the replacement series, i.e., Al, Fe and H are produced in relative abundance and undoubtedly play a dominant role in restoring the balance of charges in the lattice. The presence of these difficultly replaceable cations in "intramicellar" positions conceivably accounts, in large part, for the slow re-entrance of potassium added to acid soils. Further evidence in support of this concept appears

from the studies by Wood and DeTurk (63) who noted that fixation in colloids extracted from acid soils invariably was accompanied by release of iron.

In neutral to alkaline soils, calcium, magnesium, and sodium ions predominate, and some replacement of potassium from positions within the mica crystals is likely to be accomplished by these cations. This is borne out in experiments by Schachtschabel (53) which show that exchange occurs slowly but continuously between so-called nonexchangeable potassium of muscovite and cations in the outside solution. Martin, et al. (40) studied the reverse reaction and found that the amount of potassium fixed within 48 hours under moist conditions by a slightly alkaline soil was equivalent to the calcium, magnesium, and sodium released. Thus, two extremes are represented in the more acid soils where fixation of potassium proceeds slowly and in the alkaline soils where fixation is rapid. Between these extremes, the rates and amounts of fixation of added potassium under moist conditions may be expected to vary with the amounts of secondary micaceous minerals, the extent of weathering, pH, and other factors.

Various data which have been reported in the literature on the effect of liming on potassium fixation in soils may be partially explained on the basis of results obtained in the present study. For example, Attoe and Truog (3) found that a Spencer silt loam (pH 5.5) fixed no potassium during moist

storage for a period of 7 1/2 months. In a later study, however, Attoe (2) found that liming a Spencer soil induced measurable fixation of potassium during two years of moist storage, while the unlimed soil fixed none during the same period. It is possible that precipitation of iron and aluminum hydroxides and neutralization of hydrogen ions brought about the increase in fixation, in accordance with the theory which has been proposed.

Fixation under moist conditions has been shown to occur in illite but not in montmorillonite. Upon drying, however, fixation occurs both in the montmorillonite and illite types of clay minerals. Addition of $Ca(OH)_2$ or NaOH reduces the fixation of potassium which occurs on drying in the expanding lattice type of mineral, but increases the amount of potassium fixed by illite. Thus, when both of these minerals are present in the soil, there apparently is no way of accurately predicting whether liming would cause an increase in fixation on drying. It is apparent from this that there is a need for a method of distinguishing between the types of fixation which occur on drying in soils. A possible means of accomplishing this objective is suggested from the experiment in which the effect of diethylamine-HCl on fixation of potassium by montmorillonite and illite was shown. Addition of the amine practically destroyed the capacity of montmorillonite to fix potassium on drying, but did not affect fixation by illite

under the same conditions. Further studies of a similar nature on synthetic mixtures of the relatively pure clay minerals and on soils might lead to a qualitative or semiquantitative method for estimating the amounts of potassium fixed on drying in soils by the various clay components. It is further suggested that such a method, if devised, might serve as a simple and useful auxiliary aid in identifying the clay mineral constituents in soils.

The practical significance of certain of the findings resulting from the present investigation appear worthy of further consideration. Apparently no studies have yet been undertaken to reveal whether or not ammonium fixation, in itself, is a factor of importance with respect to the nitrogen economy in soils. It is conceivable, however, that a reserve of slowly available nitrogen might accumulate over a period of years in certain soils receiving appreciable amounts of ammonium salts. The possibility that this is true should not be disregarded in a consideration of the nitrogen nutrition of plants grown on such soils. It has been established that the fixation in nonexchangeable form of either potassium or ammonium is markedly influenced by the quantity of the other cation previously fixed. This important relationship should not be disregarded in fertilizer studies with certain soils. Fixation of potassium and ammonium ions when in direct competition also is worthy of study, since the interaction

of these cations when supplied together in mixed fertilizers has not been investigated.

A significant relation between potassium fixation in micaceous minerals and the addition of phosphate has been clearly established. This relationship might be of particular importance in modifying the available potassium status in soils containing micaceous minerals, particularly when frequent or heavy applications of phosphate have been made along with potassium fertilizer. The implications of the phosphate-potassium relationship in certain soils should be of particular interest to those who advocate building up of the reservoir of slowly available, nonreplaceable potassium in soils by relatively heavy applications of fertilizer.

This investigation has clarified the mechanism involved in the fixation of potassium in soils under moist conditions. Prior to this study, it was not known which type of mineral was concerned in the rapid fixation of potassium which had been noted in certain calcareous soils. Various experiments with soils and clay minerals have established that micaceous minerals are largely responsible for this type of fixation as well as that which takes place slowly under moist conditions in acid soils. Moreover, the knowledge concerning fixation of potassium on drying in relation to the type of clay mineral and other factors has

been extended and clarified. The revelation that montmorillonitic and illitic clay minerals respond in opposite manner to various treatments is particularly significant, since, prior to now, the effects of soil amendments such as lime and phosphate have not been interpreted in light of the clay mineral composition of the soil. This undoubtedly accounts for some of the conflicting ideas which have developed concerning the effects of various treatments on potassium fixation. The controversial question concerning the effect of lime on potassium fixation may now be further clarified as has already been indicated in discussing the results of various workers. In many cases, it is believed that the results from this study will aid in reconciling the seemingly discordant findings which have been reported in the literature concerning fixation of potassium in relation to moisture conditions, type of clay mineral, liming, phosphating, pH, and other factors.

SUMMARY AND CONCLUSIONS

Preliminary investigations to characterize the rapid type of potassium fixation which occurs under moist soil conditions revealed that this type of fixation is not limited to calcareous soils. It may also take place to a measurable extent in certain acid soils when large amounts of potassium are applied. In a calcareous Webster soil, the fixation reaction reached equilibrium within a period of 24 hours, no additional fixation occurring within eight days. The soil:water ratio was found to influence the rate of fixation during the initial stages of the reaction, but after 24 hours, this influence was only slightly apparent.

Acid extraction was found to remove completely the capacity of calcareous Webster soils to fix potassium. It was possible to restore partially the capacity of the acid-treated soil to fix potassium by raising the pH. The results obtained indicate that fixation of hydrogen ions accounts for the loss in the capacity to fix potassium which resulted from the treatment with acid.

The calcareous Webster soils also are capable of fixing ammonium ions. Results showing the relation between potassium and ammonium fixation in these soils may be summarized as follows:

1. There is a significant correlation between the amounts of potassium and ammonium fixed by soils under moist conditions.
2. The amounts of potassium fixed under moist conditions in samples containing fixed ammonium are inversely proportional to the amounts of ammonium previously fixed.
3. A similar relationship was found to exist with respect to the ammonium-fixing capacity of soils that had previously fixed various amounts of potassium, the amount of ammonium fixed being reduced in proportion to the quantity of potassium previously fixed.

It is concluded, on the basis of the definite relationships shown to exist between potassium and ammonium fixation in these soils, that these cations are fixed by the same mechanism.

During the course of these investigations, it became apparent that there is a relation between the type of fixation which occurs slowly in acid soils under moist conditions and the type of fixation which occurs rapidly in certain

calcareous soils under moist conditions. Whether the fixation occurs rapidly or slowly under moist conditions, the secondary micaceous minerals appear to be dominantly concerned. Results supporting this theory which were obtained from studies on electrodialyzed illite may be summarized as follows:

1. The capacity for fixing considerable quantities of potassium under moist conditions and on drying was induced by increasing the pH either with NaOH or $Ca(OH)_2$.
2. Phosphate additions increased the capacity of illite to fix potassium in the acid pH range, the increase being most evident in the region where maximum precipitation of iron and aluminum phosphates is known to occur. The addition of phosphate had no effect on potassium fixation when the pH value was such that no precipitation of iron and aluminum phosphates occurred.
3. Addition of fluoride ions to illite greatly increased the conversion of potassium to difficultly soluble forms, and resulted in a release of aluminum. The amount of aluminum released was related to the amount of potassium fixed.

4. Oxalate, oxine, or diethylamine-HCl did not affect fixation by illite under moist conditions, probably because steric limitations prevented their action. The possibility that hydrated potassium ions do not have free access to all of the positions capable of fixing potassium also was indicated.

In almost every case, bentonite responded differently to the treatments indicated above than did illite. Those reagents which precipitated iron and aluminum caused a reduction in the amounts of potassium fixed by bentonite on drying. These reductions were attributed to "blocking" effects which reduce the exchange capacity, to mechanical hindrance offered by the precipitates which conceivably might prevent normal closure of the flexible lattice on drying, or to both factors. The results are summarized as follows:

1. Addition of NaOH or $Ca(OH)_2$ to bentonite caused reduced fixation of potassium on drying.
2. Fixation of potassium by bentonite upon drying was reduced by addition of phosphate either as the potassium salt or sodium salt.
3. Fluoride addition gave a result similar to

that obtained with illite; it was concluded that the exchangeable aluminum existing between the sheets of montmorillonite clays also interferes with potassium fixation.

4. Oxalate greatly reduced the capacity of bentonite to fix potassium on drying, presumably due to precipitation of Al-oxalate between the expansible sheets. No clear-cut results were obtained using oxine.

5. The capacity of bentonite to fix potassium on drying is practically eliminated when rather large quantities of diethylamine-HCl are added.

On the basis of the various finding summarized above, the general conclusion is drawn that the limited fixation of potassium by acid illite under moist conditions may be attributed to the presence of aluminum, iron, and hydrogen ions in certain positions which are involved in fixation of potassium. When these ions are removed by various means such as formation of complexes, precipitation, and neutralization (hydrogen ions) the entrance of potassium into these positions is facilitated and the amount of potassium fixed is thereby increased.

The results obtained with illite and with soils lend support to the concept that fixation of potassium under moist conditions is a process of "reforming an old mineral rather than creating a new one" (63). The general concept, as applied to soils, which derives from the present study and from a consideration of pertinent evidence from other sources may be expressed as follows: The conversion of soluble potassium to non-exchangeable forms under moist conditions involves an exchange with other cations. This type of fixation is largely determined by the presence of micaceous minerals, particularly the secondary micas. The rate and extent of fixation in acid soils containing this type of mineral would be modified by such practices as liming and phosphating, because these practices effect removal of aluminum, iron, and hydrogen ions from positions potentially capable of fixing potassium. A consideration of the comparative studies on montmorillonite and illite clays indicates that some of the seemingly discordant results which have appeared in the literature dealing with potassium fixation in soils are reconcilable.

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